Solute pathways in a forested ecosystem: a drainage basin approach

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SOLUTE PATHWAYS IN A FORESTED ECOSYSTEM:

a drainage basin approach

A thesis submitted by

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ABSTRACT

Solute pathways in a forested ecosystem: a drainage basin approach

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The project sought to identify direct links between calculated hillslope solute fluxes and input/output budgets in a forested drainage basin in the United Kingdom. An intensive, short term monitoring and data collection programme was devised in order to quantify the major components of the hillslope hydrological cycle, the seasonal changes in overstorey and understorey biomass, and the chemical composition of ecologically and pedologically derived samples. Gross and net precipitation, infiltration, and soil moisture fluxes, groundwater movement and streamflow were monitored to identify the possible pathways which solutes might follow. Regular sampling of the oak and bracken vegetation, litterfall and litter enabled calculation of biomass accumulation and the rate of uptake and release of plant nutrients. The spatial variability of soil properties was quantified, but subsequent soil sampling permitted identification of seasonal trends in exchangeable cation and soil water solute concentrations. All hydrological and ecological samples were analysed for nitrogen, phosphorus, potassium, calcium, magnesium, sodium and chloride. pH, specific conductance and organic carbon were measured for selected samples. The high infiltration capacity of the soil promoted rapid vertical movement of water towards a perched water table. The presence of soil macropores and the high permeability of the soil precluded the generation of throughflow on the hillslope. Stream discharge was mainly controlled by groundwater fluxes from the perched water table. Although seasonal trends in the solute concentration of water samples and in the nutrient assimilation of vegetation were identified, isolated events, such as frassfall and storm-period litterfall, were shown to contribute significant quantities of nutrients to the forest floor. The importance of solute movement via macropores, especially phosphorus, was emphasised, with particular reference to plant availability. The relative stability of the ecosystem was reflected in the balance of the input/output budgets of solutes, with the exception of calcium and magnesium losses which were attributable to weathering of the calcareous bedrock. Bivariate and multivariate statistical analysis showed that no single biogeochemical process on the hillslope could be identified as exerting a dominant controlling influence on stream water chemistry, though isolated events may affect concentrations in the short term.

Declaration

I declare that whilst registered as a candidate for the degree of Doctor of Philosophy I have not been registered for another award of the CNAA or of a University during the research programme.

A programme of advanced studies was undertaken in partial fulfilment of the requirement of the degree. A supervised course of advanced reading was undertaken by the candidate in the first year of research. The candidate attended various conferences and study group symposia of the Institute of British Geographers and visited several research establishments for advice and instruction on techniques used during the research. The candidate received a course of instruction on the use and programming of micro and main frame computers and also tuition on the use of statistical techniques.

CONTENTS

Chapter 1.0 SOLUTE PATHWAYS IN A FORESTED ECOSYSTEM: A DRAINAGE BASIN APPROACH

		Page
1.0.	**Introduction**	1
1.1.0.	**The research model and hypothesis formulation**	8
1.1.2.	**The Investigation**	13
1.1.3.	**Hypothesis Testing**	17

Chapter 2 THE STUDY AREA, INSTRUMENTATION AND SAMPLING

2.0	**Introduction**	19
2.1	**Regional background** i) Climate ii) Geology and relief iii) Soils iv) Vegetation	19
2.2.0	**Drainage basin, Instrumentation and Sampling Methodology**	30
2.2.1	**Meteorological Station** i) Gross Precipitation ii) Air temperature + humidity iii) Windspeed + direction iv) Barometric pressure	34
2.2.2	**The Instrumented Hillslope Section (Site 2)** i) Net Precipitation - volume and chemistry ii) Infiltration iii) Soil moisture and soil water potential iv) Soil water v) Groundwater	40
2.2.3	**The Instrumented Hillslope Section (Site 1) and Streamflow**	71
2.2.4	**Vegetation and Soil Inputs** i) Vegetation ii) Soils	74

Chapter 3 ANALYTICAL TECHNIQUES

3.0	**Introduction**	84
3.1.0.	**Vegetation**	84
3.1.1.	**Sample Preparation - Vegetation**	85

3.1.2. **Acid Digestion** 85

3.2.0. **Soils** 86

3.2.1. **Sample Preparation - Soils** 87

3.2.2. **Chemical Determinations** 87
- i) Water soluble ions
- ii) Exchangeable cations: A ammonium acetate extraction; B sodium chloride extraction
- iii) Soluble Phosphate
- iv) Organic Carbon
- v) Total Nitrogen
- vi) Total Phosphorus
- vii) Cation Exchange Capacity
- viii) Soil Reaction (pH)

3.2.3. **Physical Determinations** 93
- i) Particle Size Analysis
- ii) Clay Mineralogy

3.3.0. **Water** 96

3.3.1. **Sample Preparation - Water** 97

3.3.2. **Chemical Determinations** 97
- i) Water Reaction (pH)
- ii) Specific Conductance
- iii) Dissolved Organic Matter

3.4.0. **Analytical Methods** 99

3.4.1. **Solute Analysis** 99
- i) Calcium and Magnesium
- ii) Sodium and Potassium
- iii) Ammonium
- iv) Nitrate, Nitrite and Chloride
- v) Phosphate

3.4.2. **Fluorescent Dye Detection** 103

3.4.3. **Units of Measurement** 103

3.5.0. **Validation of Results** 103
- i) Reliability of Techniques
- ii) Sample Deterioration

3.6.0. **Conclusion** 112

Chapter 4 HYDROLOGY

4.0 **Introduction** 113

4.1.0 **Hydrological Inputs** 114

4.1.1 **Litter Interception and Infiltration** 121

4.2.0 **The Soil** 126

4.2.1	**Soil Moisture**	128
4.2.2	**Flow within the Soil**	136
4.3.0	**Groundwater Hydrology**	145
4.4.0	**Surface Drainage**	150
4.5.0	**Conclusion**	158

Chapter 5.0 **WATER, SOIL AND VEGETATION CHEMISTRY**

5.0.	**Introduction**	162
5.1.0.	**Precipitation chemistry**	163
5.1.1.	**Throughfall chemistry**	172
5.2.0.	**Vegetation morphology and chemistry** i) bracken ii) oak and litterfall iii) litter	176
5.3.0.	**The Soil**	191
5.3.1.	**Spatial variation in soil chemistry**	201
5.3.2.	**Seasonal variation in soil chemistry** i) Water soluble anions ii) Exchangeable and water soluble cations iii) Field soil solutions	203
5.4.0.	**Groundwater and surface water chemistry** i) Bracken ii) Oak and litterfall iii) Litter	215
5.5.0.	**Conclusion**	223

Chapter 6.0 **ECOSYSTEM INTERACTIONS : TOWARDS AN EXPLANATION OF SOLUTE CONCENTRATIONS IN A FORESTED ECOSYSTEM**

6.0.0.	**Introduction**	227
6.1.0.	**Bivariate correlation and regression analysis**	229
6.1.1.	**Multivariate analysis**	241
6.1.2.	**Principle component analysis**	251
6.2.0.	**Conclusion**	260

Chapter 7.0 **CONCLUSION** 261

References 266

Appendix I 279

Acknowledgements 280

LIST OF FIGURES

		Page
1.1.	The Biogeochemical cycle	10
2.1	Drainage basin - site and situation map	20
2	Geology	21
3	Climatic Records for Birmingham Airport (Elmdon)	23
	A Maximum and minimum temperature	
	B Mean monthly rainfall	
	C Sunshine	
	D Evapotranspiration	
4	Soil map and legend	27
5	View of hillslope site 2	31
6	View of hillslope site 2	32
7	Experimental framework	33
8	Meteorological station	36
	A Rain gauges	
	B Recording apparatus	
9	A Resin collector	38
	B Bracken throughfall gauge	
10	Instrumented hillslope section, site 2	41
11	Oak throughfall collector	45
12	Tensiometer system	51
13	Lysimeters	59
14	A Cylindrical Corer	60
	B Lysimeters in the field	
15	Throughflow pit	65
16	Borehole water level detector	70
17	Instrumented hillslope section 1	72
18	A View across hillslope site 1	73
	B Stream and instrumentation	
19	A Stage recorder	75
	B Vacuum sampler	
20	Litter bag collector	78
21	Christmas corer	79
4.1	Monthly Rainfall 1980-81	115
4.2	Monthly antecedent precipitation index 1980-81	118
4.3	A Litter moisture characteristics	122
	B Soil moisture characteristics	
	C Maximum, minimum and mean air temperatures, Birmingham Airport, 1980-81	
	D Monthly potential evapotranspiration and cumulative potential moisture deficit, Birmingham Airport, 1980-81	
4.4	Characteristic infiltration curves	124
4.5	Representative soil profile	130
4.6	Rainfall at six hourly intervals 15 10 80 to 28 10 80	137
4.7	Antecedent Precipitation Indexes for 15 10 80 to 28 10 80 and 2 9 81 to 27 10 81	138
4.8	Soil water potentials by depth, downslope 15 10 80 to 28 10 80 139	139
4.9	Soil moisture potentials at 15cm depth 15 10 80 to 28 10 80	142
4.10	Soil moisture potentials at 30cm depth 15 10 80 to 28 10 80	143
4.11	Water table levels on the hillslope	147

4.12	Daily stream discharge for 2 9 81 to 27 10 81	151
4.13	Daily rainfall for 2 9 81 to 27 10 81	153
4.14	Soil moisture potentials at 15cm depth 4 9 81 to 25 10 81	154
4.15	Soil moisture potentials at 30cm depth 4 9 81 to 25 10 81	155
4.16	Soil moisture potentials by depth downslope 4 9 81 to 25 10 81	156
4.17	Summary of hydrological pathways	160
5.1	Rainfall and throughfall chemistry	165
5.2	Frond chemistry	180
5.3	Rhizome chemistry	181
5.4	Oak and litterfall chemistry	187
5.5	Litter chemistry	192
5.6	Soil chemistry	198
5.7	Groundwater and surface water chemistry	216
5.8	Nutrient pathways and stores	224
6.1	Principal components and the significantly loaded variables for each element.	255

LIST OF TABLES

		Page
2.1	X-ray fluorescence of Carboniferous Shales and Sandstone	26
3.1	Particle size classification	93
3.2	Percentage coefficients of variation for replicate analysis	105
3.3	Summary and accuracy of analytical techniques used	106
3.4	Cation exchange resin experiment	108
3.5	Rainfall deterioration experiment	110
4.1	Monthly rainfall of study site 1980-81 and mean monthly rainfall Atherstone Sewage Works 1941-70	116
4.2	Precipitation characteristics	120
4.3	Soil moisture characteristic during infiltration tests	125
4.4	Representative profile description	127
4.5	Summary of soil physical properties	129
4.6	Moisture retention properties of the Ah and Bt(g) horizons	132
4.7	Characteristics of dye percolation in unsaturated soil from 30 9 81 to 11 11 81	141
4.8	Monthly water balance 1980-81	159
5.1	Rainfall and throughfall characteristics	166
5.2	Correlation matrix for solute concentrations in rainfall	167
5.3	Rainfall and throughfall solute correlations	173
5.4	Correlation matrices for solute concentrations in oak and bracken throughfall	174
5.5	Total and annual nutrient inputs	177
5.6	Summary data for vegetation characteristics	184
5.7	Comparison of total tree litterfall in deciduous forests	188
5.8	Soil chemical characteristics	194
5.9	Properties of clay minerals	195
5.10	A Cross correlation matrix for variables in the A horizon	199
	B Cross correlation matrix for variables in the B horizon	
5.11	Spatial variability of the hillslope soil	202
5.12	Descriptive statistics for seasonal properties of the soil	204
5.13	Summary of exchangeable cation characteristics	209
5.14	Cross correlation matrix for variables in the groundwater	218
5.15	Groundwater and drainage channel characteristics	219
5.16	Stream water characteristics	221
5.17	Cross correlation matrix for unweighted stream water variables	222a
5.18	Nutrient fluxes and stores for 1980	225
6.1	Variables in the data matrix, variable codes and variable abbreviations	228
6.2A	Significant linear relationships between soil and vegetation chemistry	233
B	Significant linear relationships between soil and selected water chemistry variables.	234

6.3	Significant linear relationships between volume weighted stream chemistry and all other variables	237
6.4	Relationships between environmental and solute parameters in the hillslope system	240
6.5	Correlation coefficients of intercorrelated environmental variables	242
6.6	A multivariate explanation of soil nutrient concentrations	244
6.7	A multivariate explanation of hillslope and surface water chemistry	247
6.8	Principal components for each chemical element and their percentage explanation	254

LIST OF EQUATIONS

		Page
3.1	Braggs Law	95
4.1	Calculation of the monthly Antecedent Precipitation Index	117
4.2	Calculation of stemflow	119
4.3	Estimation of total pore space	131
4.4	Darcy's Law	149
4.5	Calculation of hillslope discharge	149
4.6	Water balance equation	158
5.1	The litter decomposition cycle	190
5.2	The formation of hydroxyphosphates	206

Symbols and Abbreviations

No indication of ion valency is given for the elements monitored. The following represent the symbols used in all tables:-

Ca	=	Ca^{++}
Mg	=	Mg^{++}
Na	=	Na^{+}
K	=	K^{+}
NO_3	=	NO_3^{-}
NO_2	=	NO_2^{-}
NH_4	=	NH_4^{+}
Cl	=	Cl^{-}
P	=	P

Certain standard statistical symbols and abbreviations have been employed in this study:-

$\bar{x}$	mean value
%CV	percentage coefficient of variation
%dw	percentage dry weight
SE	standard error
CI	confidence interval

Unless otherwise stated all confidence levels are 95%.

Abbreviations have been used for some of the variables monitored. These include:-

E/Exch	soil exchangeable ions
S/Sol	soil, water soluble ions
M	rainfall from meteorological station
O	oak throughfall
B	bracken throughfall
SC	specific conductance
PE	potential evapotranspiration
SMD	soil moisture deficit
API	antecedent precipitation index

Chapter 1 SOLUTE PATHWAYS IN A FORESTED ECOSYSTEM: A DRAINAGE BASIN APPROACH

1.0.0. Introduction

The solutes which are found in natural waters derive from a variety of environmental sources. The atmosphere and the weathering and erosion products of soil and rocks comprise the main contributors of solutes to natural waters. The concentration of these solutes is dependent on many environmental parameters which include climate, the activities of macro and micro flora and fauna, soil and geology characteristics and anthropogenic influences. The study of the behaviour of solutes in natural waters has traditionally been described with little reference to the interactions of these environmental phenomena, though information has been produced on the significance of various controls at different spatial scales. The transport of solutes in any environment will be a function of geomorphological and ecological processes, but a literature survey shows that the study and interpretation of water chemistry has generally been undertaken in two separate disciplines; the first based on geomorphological interpretations and processes and the second on the ecological concept of nutrient cycling. However, a common link which does exist between the two areas of study is the supply and movement of water, described as the hydrological cycle (Chorley, 1969 and Mather, 1974). The presence of water in an environment has important implications, not only for plant growth but also for the transportation of particulate matter and dissolved solids.

A global climatic approach to the explanation of geomorphic phenomena was used by Peltier (1950) who classified chemical and mechanical erosion in terms of mean annual temperatures and rainfall. This type of

approach has been used in the explanation of the chemistry of several of the worlds rivers, for example, Livingstone (1963) and Rougerie (1967). However, the description of physical processes by this method has been criticised by Stoddart (1969) and Gregory and Walling (1973) since the scale of study, definition criteria, data availability and lack of homogeneity of climato-geomorphological zones can provide imprecise information on the significance of specific controls. Further problems are encountered with changing climates and the influence of man. Gibbs (1970) broke with this traditional approach and realised that the study of the chemical composition of natural water itself, could lead to an identification of the major natural mechanisms controlling world water chemistry. He identified atmospheric precipitation, rock dominance and an evaporation-crystallization process to be the major mechanisms of control, having based his study on the relative proportion of individual ions, particularly sodium and calcium, in a water sample. Most workers in the past have acknowledged the importance of other controls on water chemistry, such as altitude and geology, for example Smyth (1913) and Anderson and Hawkes (1958). Calculation of an average chemical composition for crustal rocks and also average water chemistry enabled Anderson and Hawkes to infer the relative mobility of elements in the weathering process and thus explain solute levels in natural waters. Douglas (1972) states that the relative mobility of elements varies from one area to another depending on climate and lithology. Consequently a trend towards a reduction in spatial scales of analysis has evolved, whereby a more accurate explanation of solute behaviour could be attempted. This type of approach was adopted by Walling and Webb (1978) who studied water chemistry in the 12 tributary catchments of the drainage basin of the River Exe, United Kingdom. They developed a technique to extrapolate a large number of point measurements of solute concentrations into a map of total solute

loadings and chemical denudation which also accounted for variations in drainage basin lithology. Walling and Webb (1978) suggest a similar approach could be employed in other areas of physiographic diversity. Many other experiments have used the drainage basin as a fundamental unit of study in the analysis of geomorphic processes and water chemistry; for example, the Institute of Hydrology (1977) at the Plynlimon catchments, Ternan and Williams (1978), investigating hydrological pathways and granite weathering, and Dearing et al (1982) who used a small drainage basin to provide detailed solute and sediment budgets. The usual research procedure has been to identify solute loadings in precipitation and the subsequent outputs in stream water. The intermediate processes such as evaporation, soil moisture fluxes and groundwater changes are monitored on a hillslope scale. Intensive instrumentation of a hillslope section within the drainage basin provides detailed and often continuous information of solute chemistry and water fluxes, which helps to provide a more precise explanation of solute concentration and transport through a drainage basin; for example, Nortcliff and Thornes (1978, 1979). Hillslope processes which influence the chemistry of natural water have been studied in detail by many workers, for example, Weyman (1970), Knapp (1973), Atkinson (1978) and Whipkey and Kirkby (1978) investigated the lateral movement of water within the soil matrix. Burt (1979) and Burt et al (1981) identified the magnitude and frequency of solute removal by this process in an attempt to explain stream water chemistry and the rate of hillslope solutional denudation. Previous work by Walling and Foster (1975) had only inferred the removal of solutes from hillslopes, by analysis of stream water chemistry. An understanding of hillslope processes has been aided by laboratory experiments which have involved the use of soil columns and lysimeters and other similar methods to investigate processes such as infiltration, water movement and run-off under controlled conditions.

Examples of this type of study include those of Colman (1946), who investigated drainage from a lysimeter under controlled soil moisture tension, Bouma et al (1977) and Bouma et al (1979), who explained water movement through soils with particular reference to hydraulic conductivity and macropore flow. In addition Omoti and Wild (1979) used fluorescent dyes to mark the pathways of solute movement through soils under leaching conditions. Laboratory experiments do help to explain complex processes but Ackermann (1966) states that they fail in certain important respects to represent field conditions. The current trend towards an intensive, short term monitoring programme on the hillslope scale, within the context of a drainage basin, emphasises the fact that solute dynamics may be successfully accounted for by microscale investigations. Intensive studies of this type allow the characterisation of most of the factors which may influence the chemistry of natural waters. Such studies have enabled the formulation of models which can predict stream water chemistry, for example Johnson et al (1969) and Foster (1980). The use of drainage basins in geomorphological and hydrological research has been criticised, with the main objections being cost, their unrepresentativeness, lack of application to other areas and the difficulty of assuming the basin is watertight (Ackermann, 1966). However, Hewlett et al (1969) state that much of the basic hydrologic knowledge has come from well planned watershed experiments and recommended their continued usage.

The second approach to the study of solute dynamics is based on an analysis of the ecological processes of nutrient and biogeochemical cycling. Work in the 19th century by naturalists such as Humboldt and Koppen defined major plant zones (for example, Tundra, Boreal and Mediterranean) on the basis of the type of soil and climate and also on the vegetation assemblage; Tivy (1971) describes these broad classifications. The

development of the ecosystem concept (Tansley, 1935) provided a platform for an investigation of the complex interactions between plants, animals and their environment. The boundaries of ecological units are difficult to identify since environmental characteristics may change over time, for example, climate, plant succession and the influence of man. Ovington (1962) states that it is unlikely that universally acceptable categories of ecosystems with discrete boundaries will ever be recognised. Evans (1956) notes that any ecological unit can be defined as an ecosystem, for example, the entire biosphere, the soil or even a single acorn. Odum (1963) defined an ecosystem as an open physical system, since energy and matter are both received from external sources and exchanged between adjacent systems. Fluxes of water and solutes are controlled by a vast number of variables including, biota, geology, climate and season (Likens et al, 1977). Both living and non-living components of the ecosystem are important for the regulation of fluxes which are identified in the nutrient and biogeochemical cycles (Odum, 1963). The term 'forest ecosystem' is a broad generalisation for all ecosystem types with a dominant tree species, examples of which may be coniferous forests, deciduous woodland or hardwood forests. Forest ecosystems are also classified according to climate and world location whilst their size may vary from a few trees to vast areas of forest, such as the Black Forest in West Germany.

Most previous studies of forested ecosystems have investigated specific aspects of component interactions in order to explain a particular ecological process. The nutrient content of rainfall has been reported by Allen et al (1968), whilst the interception properties of vegetation have been assessed by Helvey and Patric (1965a), Carlisle et al (1965) and Argent (1979). The loss of moisture to the atmosphere by transpiration has been studied by Calder (1977) and Roberts et al (1980). Several

workers, including Penman (1949) and Hall and Heaven (1979), have described the seasonal soil moisture deficits which are a result of evapotranspiration. The modification of precipitation chemistry by the vegetation canopy has initiated several studies on throughfall and stemflow, for example, Carlisle et al (1966b), Eaton et al (1973), Bernhard-Reversat (1975) and Tollenaar and Ryckborst (1975). The productivity of vegetation is usually measured by harvesting plant growth to estimate biomass (Newbould, 1967, 1968, and Callaghan et al, 1981), or the litterfall method which assesses annual productivity (Newbould, 1967). The nutrient content of litterfall maintains an important supply of minerals to the soil surface, (Gosz et al, 1972, and Brassell et al, 1980) and the subsequent decomposition of litter provides a gradual supply of solutes to the soil (Frankland, 1976). Uptake of nutrients from the soil has been reported by Russell (1961) and Saunders and Metson (1971), whilst Hunter (1953) compared the nutrient content of vegetation with that of different soil types.

The in situ nutrient cycling and ecology of individual species has been the subject of intensive investigation by many workers, for example, Watt has investigated bracken and its rhizomes with reference to community structure (1947), frost (1950), competition (1955), growth (1956), as well as more general aspects of the species (1940, 1945, 1964, 1976). The study of oak has received attention from Bocock (1963), Carlisle et al (1965, 1966a, 1966b) and Morris and Perring (1974).

Examples of the ecosystem approach which identify nutrient budgets, not only for the inputs and outputs, but also for the internal organisation of the system, including vegetation and soil, are rare in the literature. Perhaps the best known and most comprehensive study is that of the

Hubbard Brook Experimental Forest in the White Mountains of New Hampshire; this work investigates hydrology and input-output chemistry as well as the structure, function and dynamics of the forest ecosystem itself. The ecosystem unit of study is a drainage basin with the vertical and horizontal boundaries defined by biologic activity and the drainage of water (Bormann and Likens, 1967). Since its inception in 1955 a large number of experiments have been performed and Likens et al (1977) and Bormann and Likens (1979) have summarised the major findings of the Hubbard Brook study. Studies have included an investigation of the effects of forest removal on solute and sediment pathways within a drainage basin. Hornbeck et al (1970) showed that a period of time was required for the soil structure and chemistry to deteriorate before significant increases in stream solute concentrations and sediment volume were observed. However, none of the Hubbard Brook studies have investigated, in detail, the movement of water within the soil matrix and the fluxes in exchangeable and water soluble ion concentrations. No other comprehensive research similar to that of the Hubbard Brook study is known to exist in the literature.

There has been an increasing awareness that solute chemistry and pathways within an environment should be the subject of multidisciplinary research. Douglas (1972) writes 'a geographer can both benefit and learn from association with the many interdisciplinary projects investigating aspects of the solusphere'. Whilst Gregory and Walling (1973) state that it is now very difficult to envisage the existence of discrete disciplines in the study of earth sciences and Walling (1980) presents a multidisciplinary conceptual model to describe water quality in a catchment ecosystem. The systems approach to environmental science also illustrates the need for the study of a range of disciplines before an understanding of environmental systems can be gained, for example, Jeffers (1978) and Huggett(1980).

The use of the drainage basin as a fundamental unit of study in environmental disciplines has become increasingly popular in the last decade. Nutrient budgets and water fluxes can be closely monitored within a defined area where physiographic variability can be identified.

1.1.0. The research model and hypothesis formulations

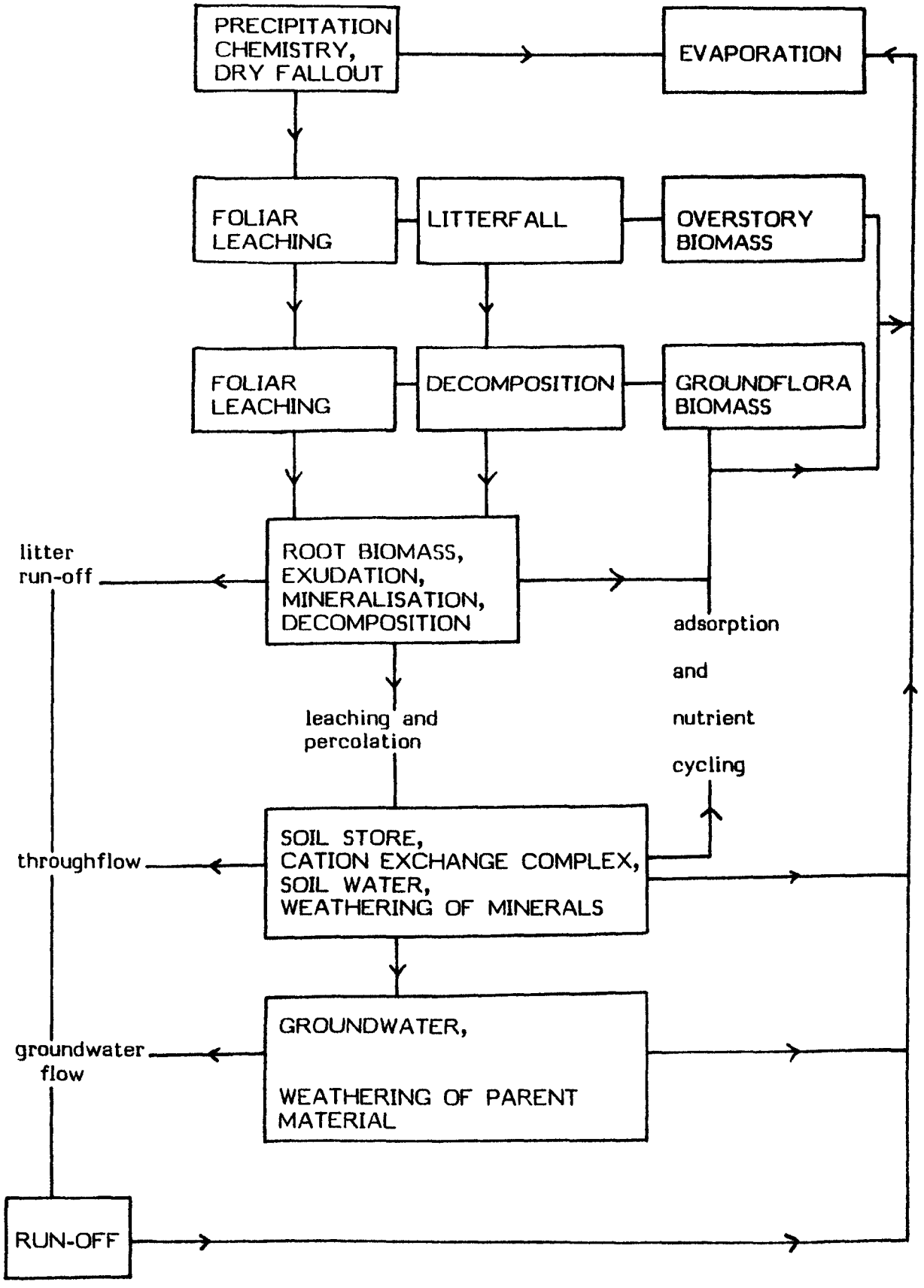
It has been shown that previous work in the field of solute dynamics has been insufficiently interdisciplinary in approach and the present study aims to combine the environmental disciplines of geomorphology, hydrology, soil science and ecology in order to provide a common link between the disciplines, in an attempt to assess the influence that vegetation has on solute chemistry and the pathways which water follows within an ecosystem. The current investigation was prompted by the comments of Ovington (1962) who wrote that 'present knowledge of the quantitative aspects of the processes concerned in forest dynamics are unfortunately far too scanty and disjointed'. These comments have been supported by Douglas (1972) who showed there to be little information available for the interpretation of river water quality with respect to nutrient cycling and Trudgill et al (1980) who stated that 'the precise relationships between input waters, solute uptake, flow rates, flow routes and solute production are imperfectly understood'.

In an environmental study there should be a logical flow of ideas which creates a properly structured experiment. The first stage in this experiment is the creation of a conceptual model of the processes or relations of interest which would ultimately be supported or refuted by the experiment. All models are abstractions and simplifications of reality and in environmental studies a model that completely describes the complex system involved would have hundreds of simultaneous partial differential equations with time lags and many parameters (Green, 1979).

Simplification is therefore both legitimate and necessary and it is not perfection which is aimed at but adequacy in the description of processes and relations. The model described for this experiment derives from previously developed theories, general scientific principles and, more informally, from the results of a study by Foster and Grieve (1981). The model was essentially a combination of the hydrological and nutrient cycles and the suppositon was made that the flux of solutes within an ecosystem was inextricably linked with the movement of water at different stages in the hydrological cycle. Models which integrate the hydrologic and nutrient cycling approaches have been described by Huggett (1980) and Walling (1980) and whilst the interactions are known to exist few attempts have been made to characterise their magnitude and direction. The interaction of the biosphere and hydrosphere form the basis of this biogeochemical model and the storage components and flows of the general model are shown in Figure 1.1.

The model envisages that the dissolved solids content of precipitation is significantly altered when it passes through the vegetation canopy due to foliar leaching. When this throughfall infiltrates the litter layer and percolates into the soil, solutes may be stored in the exchange complex or soil water, or may be transferred to the groundwater. Plants draw on the nutrient reserves in the soil and the minerals taken up are temporarily immobilised in the biomass stores. They are returned to the soil via leaching, litterfall, root sloughage, exudation and by decomposition of the dead vegetation. The nutrients in the basin may be depleted or transformed by chemical processes to unavailable forms by erosion and by losses to the stream via throughflow, pipeflow, litter run-off and groundwater flow. Weathering of minerals in the soil and groundwater stores and evaporation also influence the concentration of nutrients in the system.

Figure 1.1 **BIOGEOCHEMICAL MODEL**



The construction of this general ecosystem model allowed the formulation of a general research hypothesis which postulated that there was no interaction of processes between the biosphere and the hydrosphere. Previous work, for example, Carlisle et al (1966a, 1966b) and Likens et al (1977) has already demonstrated the interaction of biological and hydrological processes and therefore the general hypothesis could be immediately rejected, although the interactive processes were monitored to determine the magnitude and frequency of such interactions. Specific hypotheses which aimed to test relationships in more detail were therefore formulated. The role of vegetation, particularly groundflora, has in the past been underestimated in the study of nutrient cycles and solute movement. A number of working hypotheses were therefore derived from the biogeochemical model to identify the short term and seasonal trends of solute concentrations in the drainage basin. The first hypothesis postulated that:-

> There was no seasonal change in the chemical composition and concentration of solutes in a drainage basin.

Deciduous vegetation by definition, exhibits a seasonal pattern of growth, which can be easily monitored. This research seeks to identify any similar seasonal trends in soil and water chemistry.

The second hypothesis proposed that:-

> Precipitation chemistry was not modified when it passed through the canopies of different vegetation species.

Such changes in precipitation chemistry have been identified, for example by Carlisle et al (1966b) and Eaton et al (1973). However, it was the magnitude of the changes made by the different vegetation species which were of particular interest in the present study.

The third hypothesis postulated that:-

> The chemistry of soil exchange sites and soil water was not altered by the growth of vegetation.

Russell (1961) and Saunders and Metson (1971) reported the seasonal uptake of nutrients in arable and grassland situations but no researchers, with the exception of Weaver and Forcella (1979), have reported comparable results for soils under semi-natural woodland.

The fourth hypothesis develops this concept further:-

> The spatial variability of soil properties does not mask the seasonal variations in soil properties.

Frankland et al (1963) and Ball and Williams (1968) were unable to identify seasonal trends in soil properties because the spatial variability of their sites was greater than any seasonal change which was monitored. Their findings are endorsed by Beckett and Webster (1971) who found a large proportion of soil variability within a study site can occur in an area as small as a metre square.

The fifth hypothesis was based upon recently published findings which attribute rapid water flow in soils to the presence of macropores, for example, Scotter (1978) and Germann and Beven (1981). The extent to which vegetation may influence the solute concentration of these rapid flows was postulated thus:-

> The seasonal growth of vegetation does not exert an influence on the magnitude and frequency of solute transfer within the soil matrix on the hillslope scale.

The remaining hypotheses are related to stream water chemistry. The seasonal fluction in the concentration of certain solutes in stream water

has been linked to the uptake of the nutrients by vegetation, for example, Likens et al (1977) and Reid et al (1981) but no direct evidence of the relationship can be found in the literature.

The sixth hypothesis postulates that:-

> The timing and magnitude of solute concentrations in stream water was not influenced by changes in the soil exchange complex and nutrient cycling.

The seventh hypothesis was related to the denudation of the basin:-

> The output of dissolved solids in streamwater was not derived from the chemical weathering of minerals within the drainage basin.

The stability of the ecosystem is often reflected in the balance of the input/output budgets of ions and therefore the amount of solutes lost by weathering of minerals from the drainage basin was of relevance to this study.

1.1.2. The Investigation

An investigation was established to test the working hypotheses and critically assess the conceptual biogeochemical model. This investigation did not qualify as an experiment as Church (1981) describes an experiment to be a controlled interference of the natural condition of the environment in order to obtain results about a limited subset of processes. However, Church does argue that those investigations which employ statistical methods to control environmental variability are also true experiments. Therefore under the latter definition the present investigation does qualify in some respects as an experiment. Figure 1.1 presented the simplified

subset of processes and this experiment placed them within the context of the drainage basin to provide a convenient and acceptable framework of study. The choice of drainage basin for the present research was governed by the need to fulfil certain requirements:-

1) Proximity to the centre of study and access to the land.
2) A dominant vegetation of deciduous woodland.
3) A clearly defined, small, drainage basin with known geology to assess the subsurface boundaries of the basin.
4) Minimal human interference - in terms of land management and vandalism.

A basin which fulfilled these requirements had been located by Foster and Grieve (1981) and the present study formed part of a wider investigation of solute dynamics and erosional processes in the drainage basin. A study of this type should ideally be extended over a period of several years to obtain results which are not biased by temporal variability. However, such an extended period of study was not possible due to the time limitations of the research programme. Therefore a short intensive monitoring schedule was devised with emphasis on the continuous monitoring of as many of the processes as possible (Ackermann, 1966). Two main considerations were identified in the development of the experiment; that is the chemistry of the water, soil and vegetation and secondly the fluxes of water within the ecosystem.

A wide variety of elements have been monitored in the past, in the study of solute dynamics, depending on the nature of the investigation. Ternan and Williams (1978), for example, monitored fluxes of silica as an index of granite weathering, whilst Trudgill et al (1981) investigated the loss of

nitrate from a deciduous woodland. The requirement of the present study was to monitor those elements whose pathways might be influenced by the growth of vegetation. Consequently the three major plant nutrients, nitrogen, phosphorus and potassium were chosen to represent those ions whose behaviour may be indicative of vegetation processes. Calcium and magnesium, as plant micronutrients and common constituents of the soil and geology, were chosen to represent ions whose concentrations could be influenced by weathering and vegetation processes. Sodium and chloride represented those ions whose movement and behaviour in the ecosystem were less influenced by vegetation and soil processes.

Nitrogen occurs mainly as nitrate and ammonium in a natural environment and whilst ammonium has not normally been routinely monitored in solute studies, Likens et al (1977) found that ammonium was the second most abundant cation in precipitation falling in the Hubbard Brook ecosystem. Analysis of water samples showed ammonium to occur in significant quantities in precipitation, throughflow and soil water samples for the present study catchment. Nitrate and ammonium are both taken up by plants from the soil solution and these ions were therefore determined independently. A more complete assessment of total nitrogen was made by also monitoring nitrite levels. Plant available phosphorus occurs principally as orthophosphate in the soil and, although not present in large quantities in the soil, is an essential nutrient. All determinations were made for phosphorus to avoid any misunderstanding over the expression of the type of orthophosphate detected. Potassium is not a constituent of plant fabric, being found in cell sap, but is still an essential nutrient. Several workers have shown potassium to be a readily soluble ion, which is easily leached from vegetation. Consequently the associated nutrient cycle is of particular interest in the study of solute dynamics.

Calcium and magnesium are minor plant nutrients. Both are divalent cations and Russell (1961) shows their behaviour in the soil system to differ from that of monovalent cations such as potassium. Calcium and magnesium are usually the most abundant of the exchangeable cations in the soil and their determination provides an indication of the stability of the soil system.

The role of sodium in plant nutrition is less clearly understood and whilst not an essential nutrient it is taken up by plants which do appear to have improved growth in its presence (Russell, 1961). Sodium was therefore chosen to represent an ion whose pathways may be less influenced by vegetative control. Chloride levels were monitored since large quantities of chloride have been identified in precipitation, particularly in throughfall (Junge, 1963, and Stevenson, 1968). In vegetation, chloride behaves in a similar manner to potassium, being an osmotic regulator in cell sap. As an anion it occurs mainly in the soil solution and its pathways are thought to be largely determined by the fluxes of water in the ecosystem.

The phenomenon of acid rain and its subsequent effect on ecosystem processes is well documented, for example, Grannat (1972), Likens et al (1979) and Martin (1979). The drainage basin chosen is situated near several of the power stations of the Trent Valley (Pearce, 1982) which are likely sources of acid pollution. Therefore the acidity of all water samples was monitored in order to evaluate the possible effects of acid rain on the ecosystem. The specific conductance of water samples was also measured as an indicator of ionic concentration in solution, although its use as an indicator of total dissolved solids in an acid environment has been questioned (Foster et al, 1981 - see rear wallet).

Data concerning the concentrations of sulphate, silica, iron, aluminium, manganese, carbonate, bicarbonate and dissolved organic matter were also available for reference from the original experimental site of Foster and Grieve (1981).

Figure 1.1 identified the processes which were thought for a priori reasons to be important in the evaluation of solute pathways in the study basin. The characterisation of these processes over the entire drainage basin was not possible and therefore a hillslope section, which was fairly representative of the soil and vegetation type found in the basin, was chosen for intensive monitoring of processes. Chapter 2.0 describes the instrumentation of this hillslope section and the collection procedures which were employed. The site was visited on a weekly basis for the collection of water samples; however, time constraints and the possibility of site destruction limited the sampling of soils to fortnightly intervals and the sampling of vegetation to intervals which varied according to the growth characteristics of the vegetation and season. The study commenced in June 1980 and continued until the end of December 1981, incorporating 76 weekly sampling sessions and 19 vegetation sampling periods.

1.1.3. Hypothesis Testing

The continuous monitoring of nutrient concentrations over time would provide trend plots which could be subjected to harmonic analysis to identify any seasonal trends. The calculation of nutrient budgets in gross and net precipitation would enable assessment of the influence of tree and groundflora canopies on the chemistry of precipitation whilst the use of simple linear regression analysis aimed to measure the strength and direction of these relationships. Bivariate regression and multiple

regression analysis was employed to identify those vegetation parameters which possibly influenced the exchangeable and water soluble ion concentrations in the soil. A detailed soil survey and analysis of soil samples were undertaken to identify the variability of the hillslope site and thus establish confidence levels upon which seasonal variations in soil properties could be superimposed. Multiple regression analysis using vegetation parameters as independent variables aimed to explain the variance in soil water extracts, subsurface water samples and stream chemistry. The calculation of input-output budgets for each element monitored within the drainage basin would enable an assessment of the amount of weathering and subsequent denudation of the catchment.

The present research aimed to test the conceptual model presented in Figure 1.1. using principal component analysis in an attempt to provide statistical evidence for the behaviour of solutes and the interaction of processes within the drainage basin.

Chapter 2 THE STUDY AREA, INSTRUMENTATION AND SAMPLING

2.0 Introduction

The drainage basin is initially considered in a regional context to identify long term characteristics such as climate, geology and relief, soils and vegetation. The following sections describe the instrumentation used to identify water fluxes and chemistry at different stages of the drainage basin hydrological cycle. The sampling procedures used to obtain vegetation and soil samples representative of the study site are then described.

2.1.0. Regional Background

The drainage basin chosen for this investigation lies 2.5km south-west of Atherstone in North Warwickshire (SP290960) and is situated on a private estate. It is a second order drainage basin and covers an area of 95.16ha (Figure 2.1). Estate records and maps show that the area has been mainly under woodland since at least 1740, with the exception of a period of cultivation in the mid-19th century (Dearing et al, 1982). Replanting occurred in the later part of the century and since this time the deciduous woodland has developed 'semi-naturally' with minimal woodland management. The central part of the drainage basin overlies the Upper Coal Measures (Figure 2.2) and this area was strip mined in 1950-54. The soils were subsequently reclaimed and a mixed coniferous plantation established (293960). The disturbing effect of these actions on the evolution of the drainage basin would have had unknown repercussions on an experiment of this type. Consequently all measurements were taken upstream of this disturbed area and Figure 2.1 shows the area of the sub basin.

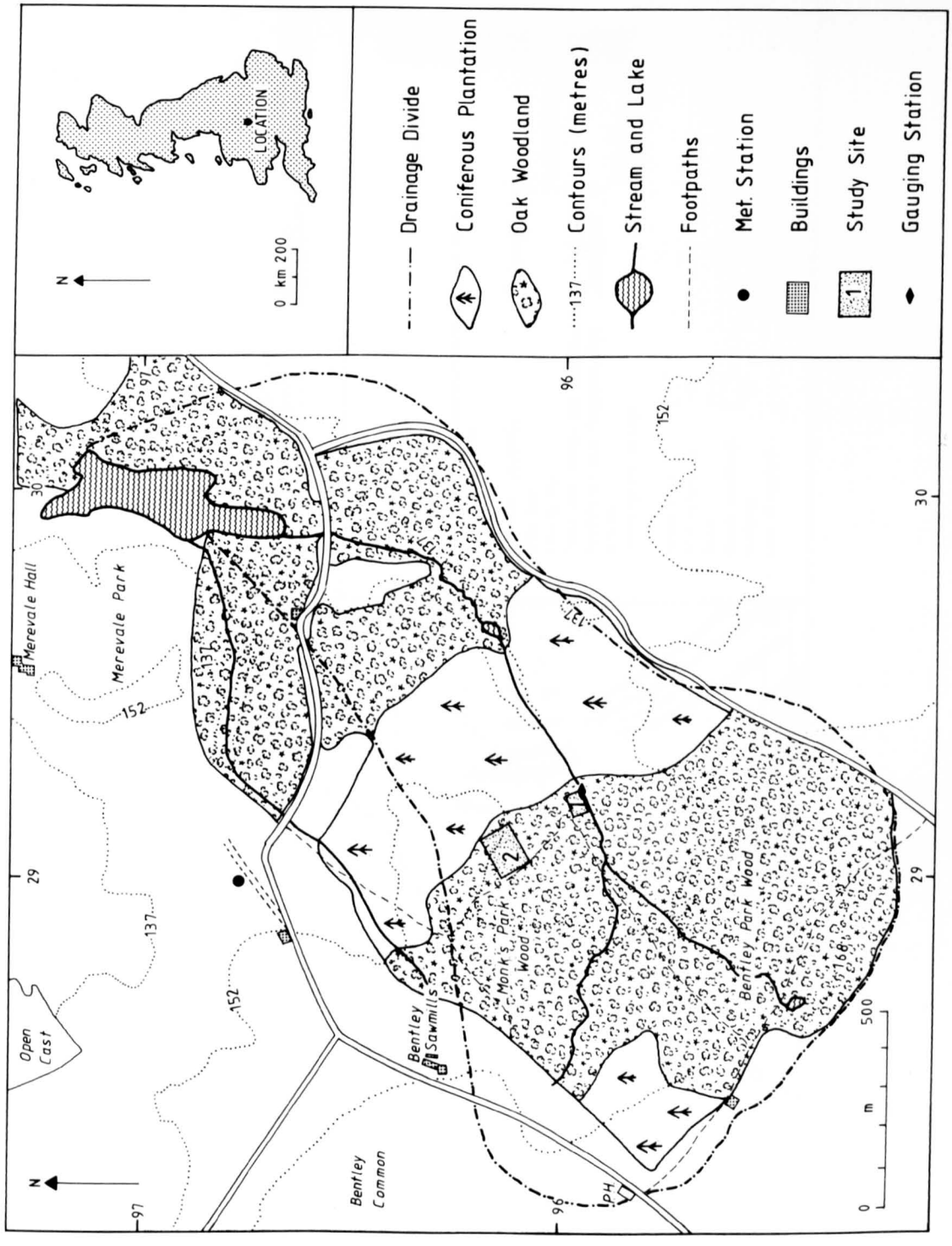


Figure 2.1 Site and situation map

Figure 2.2 Geology

The climate, geology, relief, soils and vegetation are described for the drainage basin and the surrounding area. The soils and vegetation of the hillslope site are considered in detail in Chapter 5.

i) Climate

Figure 2.3 illustrates some long term meteorological data from Birmingham Airport (170833) 97.2m O.D. which lies 18.5km south-west of the drainage basin. Generally the climate reflects the inland position of the area (Figure 2.1) having a small range of temperatures and an even, temporal distribution of rainfall. The area is defined as hemioceanic by Bendelow and Hartnup (1980) or humid temperate with a cold season by Gregory (1976).

Mean temperatures range from 3.1^{0}C in January to 15.9^{0}C in August and this restricted range of temperature illustrates the ameliorating effect of the inland position (Figure 2.3A). The critical temperature for plant growth is 6^{0}C in a humid temperate climate and the data shows that the length of growing season for this area is 254 days. The earliest frost usually occurs around 15th October and the last frost around 6th May (Whitfield and Beard, 1980). Mean monthly rainfall figures from 1941-1970 are illustrated in Figure 2.3B which shows a fairly uniform distribution of rainfall throughout the year with a 30 year mean annual average of 672mm. A monthly maximum of 71mm occurs in August and precipitation in October (56mm), November (69mm) and December (60mm) is maintained by depressions from the west supplying frontal rain. Figure 2.3D illustrates the mean monthly potential evapotranspiration (P.E.) and cumulative soil moisture deficit (S.M.D.) for 1941-70. P.E. is defined as the loss of water

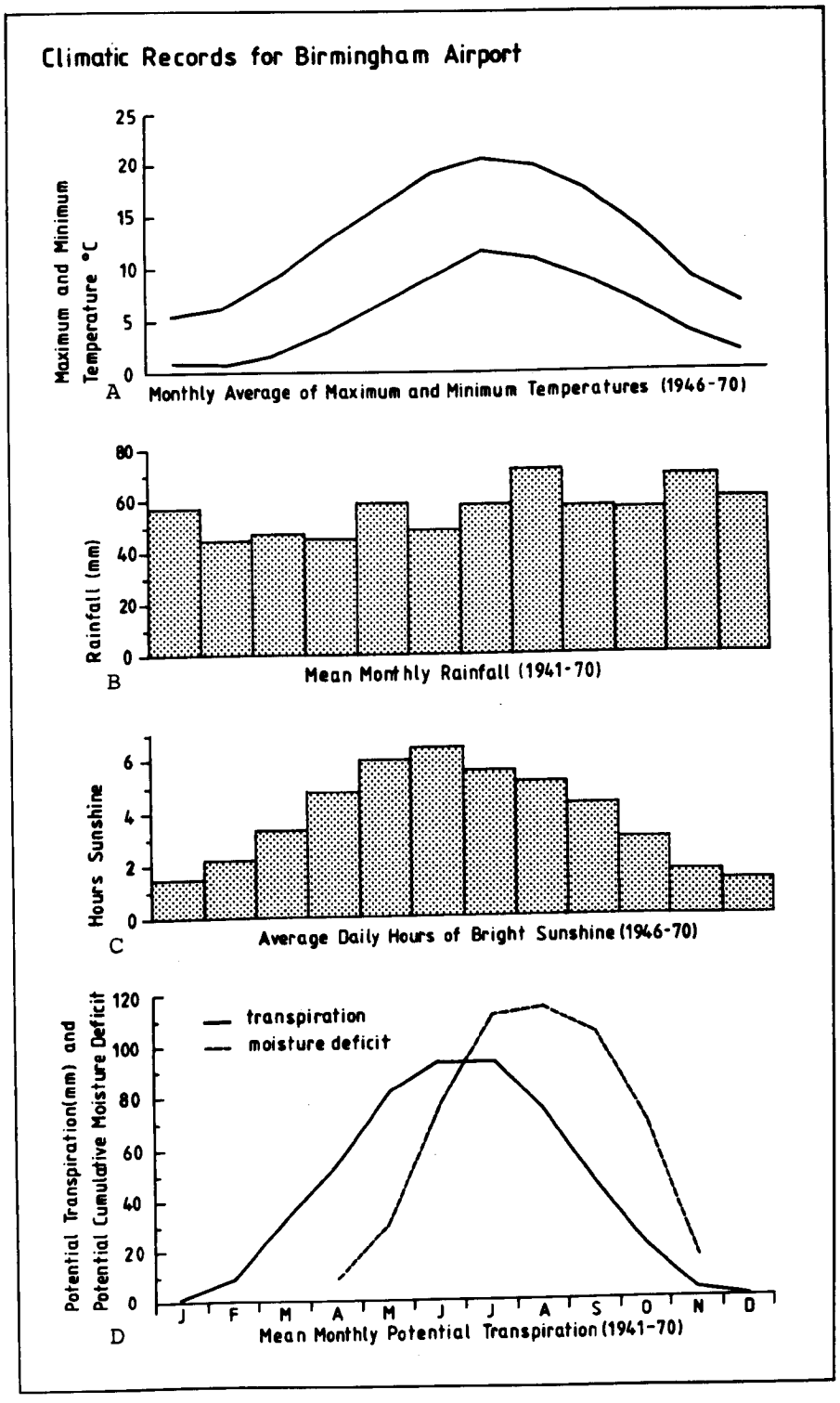

Climatic Records for Birmingham Airport
Maximum and Minimum Temperature °C
25
20
15
10
5
0
A
Monthly Average of Maximum and Minimum Temperatures (1946-70)
Rainfall (mm)
80
60
40
20
0
B
Mean Monthly Rainfall (1941-70)
Hours Sunshine
6
4
2
0
C
Average Daily Hours of Bright Sunshine (1946-70)
Potential Transpiration(mm) and Potential Cumulative Moisture Deficit
120
100
80
60
40
20
0
transpiration
moisture deficit
J F M A M J J A S O N D
D
Mean Monthly Potential Transpiration (1941-70)

Figure 2.3

that occurs from an extensive closed cover of vegetation that never suffers from a lack of water (Mather, 1974). Maximum monthly values occur in June and July (93mm), with a value of only 1mm in December and January. The mean monthly potential S.M.D. was calculated as the difference between precipitation and P.E. and shows a deficit from July to December. A maximum potential deficit is achieved in August but the deficit is quickly replenished in autumn and winter months when rainfall exceeds P.E. Figure 2.3C shows the mean daily hours of sunshine at Birmingham Airport for 1946-70. Maximum hours occur in June (6.5 hours) and minimum in December (1.4 hrs). The amount of solar radiation affects temperature and evapotranspiration, which are considered in later sections.

Bendelow and Hartnup (1980) provide a climatic summary for the region; the thermal characteristics are moderately cool and the moisture regime is characterised as slightly moist, with an actual maximum soil moisture deficit ranging between 100 and 180mm. The area is unexposed with an annual average windspeed of less than 4.8m sec^{-1}. The climate has cold winters, warm summers and a short intense growing season.

ii) Geology and Relief

The drainage basin lies within a lowland area between two rivers, the Anker to the north-east and the Tame to the south-west, both major tributaries to the River Trent. The maximum altitude of the region is 175m at Bentley Common (254962) and a minimum of 64m in the Tame valley. The catchment lies at approximately 130m O.D. and the area has a relative relief of approximately 40m with an average channel slope of 0.046 (Foster and Grieve,

1981). Whitfield and Beard (1980) divide the geology of the region into three broad morphological units, consisting of an uplifted block of Carboniferous and Cambrian sediments surrounded by Keuper sandstones of the Triassic period (Figure 2.2). Stockingford shales represent the Cambrian rocks and form a synclinal outcrop of steeply dipping beds as illustrated in the Merevale section of Figure 2.2 Sills of Ordovician diorite intrude into the Cambrian sediments and form prominent hogsback ridges. The Warwickshire coalfield lies to the south-west of the Stockingford shales and consists of Carboniferous Upper Coal Measures and Keele beds interbedded with mudstone, clay shale and subordinate bands of Spirobis limestone. Triassic Keuper Marl and sandstone surround the Cambrian and Carboniferous outcrops. The Triassic rocks are largely covered by drift deposits of Pleistocene age. Wolstonian deposits consist of tills, glaciolacustrine clays and outwash gravel. Glacial ice did not cover the area during the Devensian period and deposits are mainly sands and gravels. Solifluction was widespread at this time and large areas in the region are covered by thin layers of highly mixed periglacial slope deposits. The drainage basin lies across the Carboniferous and Cambrian outcrops with the upper section of the catchment being underlain by sandstones and shales of the Keele beds which bear superficial deposits of Wolstonian boulder clay. The results of X-ray fluorescence tests on the two main rock types found within the upper catchment are shown in Table 2.1 (Foster et al, 1983 - see rear wallet).

Table 2.1 **X-Ray Fluorescence of Carboniferous Shales and Sandstone**

Sandstone

Major	K	Si	Ti	Fe
Minor	Al	Ba	Ca	
Trace	Zr	Rb		

Shale

Major	Ca	Ti	K	Fe
Minor	Si	Al		
Trace	Ba	Zr	Rb	

Many other trace elements were also detected in both samples including Mg, P, S, Cl, Cr, Mn, Ni, Cu, Zn.

iii) Soils

Figure 2.4 shows the soil mapping units in the drainage basin and surrounding area identified by Whitfield and Beard (1980). The soils are closely associated with the surface drift deposits and the outcrops of Carboniferous sandstone. Map units such as Rufford, Baxterley and Bardsey occur on the drift areas which are underlain by mudstones and shales. These first two types are argillic and all three types may be wet for long periods during the winter. Gleying is shown in the majority of soil horizons within 40cm depth (Robson and Thomasson, 1977). Where the underlying geology is sandstone typical brown earths of the Shifnal and Rivington units are mapped and a gleyic brown earth of the Melbourne series is also identified. A complete description of the soils in Warwickshire is provided by Whitfield and Beard (1980) and a description of the Melbourne soil series found on the hillsope study site is presented in Chapter 5.

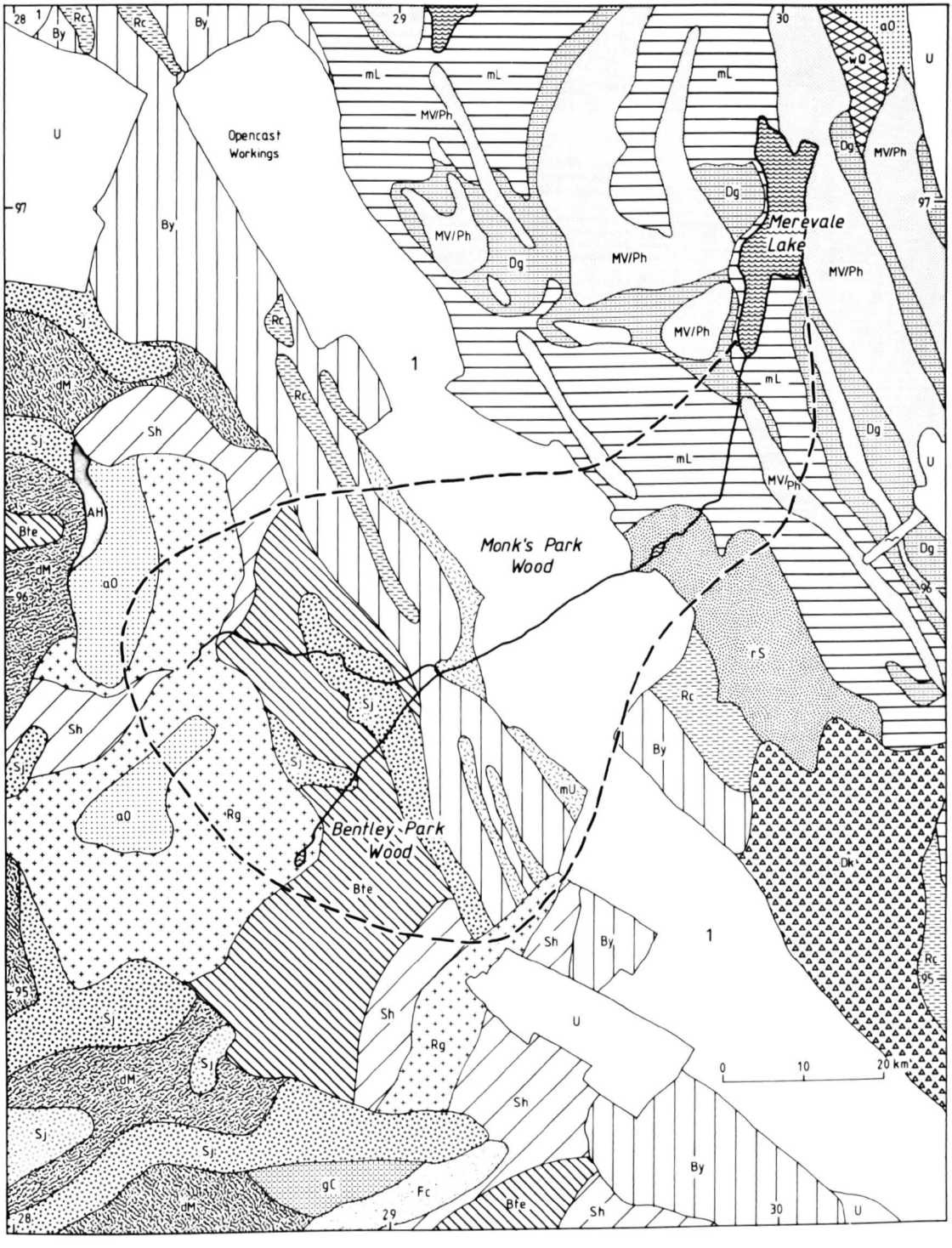


Figure 2.4 Soil map. (Whitfield and Beard, 1980)

SOIL GROUP	SOIL SUBGROUP	LITHOLOGY	SOIL SERIES	MAP SYMBOL
Rankers	Brown rankers	Fine loamy or fine silty over Lower Palaeozoic mudstone or sand stone.	POWYS	Ph
Brown earths (sensu stricto)	Typical brown earths	Coarse loamy; drift (glacio fluvial deposits derived mainly from Triassic rocks)	WICK	wQ
		Coarse loamy over reddish Carboniferous sandstone	SHIFNAL	Sj
		Coarse loamy over Carboniferous sandstone	RIVINGTON	Rc
		Coarse loamy over medium grained reddish Devonian sandstone	ROSS	rS
		Fine loamy or fine silty over Lower Palaeozoic mudstone or sandstone	DENBIGH	Dg
	Gleyic brown earths	Coarse loamy; drift (glaciofluvial deposits derived mainly from Triassic rocks)	ARROW	aO
		Coarse loamy over Carboniferous sandstone	MELBOURNE	mU
Argillic brown earths	Stagnogleyic argillic brown earths	Fine loamy over clayey;drift over reddish Carboniferous mudstone or clay shale	DODMOOR	dM
		Coarse loamy over clayey; drift over reddish Carboniferous mudstone or clay shale	GATACRE	gC
		Fine loamy over clayey; reddish till (derived mainly from Triassic rocks)	FLINT	Fc
		Coarse loamy over clayey; reddish drift (glacio-fluvial deposits over till derived mainly from Triassic rocks)	ASTLEY HALL	AH
		Fine loamy over clayey; drift over Lower Palaeozoic mudstone or clay shale	MEREVALE	mL
Brown podzolic soils	Typical brown podzolic soils	Loamy-skeletal over intermediate and basic igneous rocks or Head containing those rocks	MALVERN	MV
Stagnogley soils	Typical stagnogley soils	Fine loamy over clayey; drift over reddish Carboniferous mudstone or clay shale	BAXTERLEY	Bte
		Fine loamy over clayey; reddish till (derived mainly from Triassic rocks)	SALOP	Sh
		Coarse loamy over clayey; reddish drift (glacio-fluvial deposits over till derived mainly from Triassic rocks)	RUFFORD	Rg
		Fine loamy over clayey; drift (till or Head derived mainly from Carboniferous rocks)	DUNKESWICK	Dk
	Cambic stagnogley soils	Fine loamy over clayey; drift over Carboniferous clay shale or silty shale	BARDSEY	By

Undifferentiated alluvial soils ~

Reclaimed areas 1

Unsurveyed areas including principle urban areas and disturbed ground U

iv) Vegetation

The vegetation within the upper section of the drainage basin consists of deciduous woodland, a coniferous plantation and grassland. The coniferous plantation of Larix europaea (European larch) and Pinus sylvestris (Scots pine) is approximately fifty years old and lies in the south-west corner of the catchment (275948) covering 7.5% of the upper section area. 14.1% of the upper section is under permanent pasture and the remaining 78.4% is covered by deciduous woodland dominated by Quercus petraea (Sessile oak) which was probably planted in the mid-19th century. An attempt to estimate the age of the woodland was made using two dendrochronological methods. An increment core was taken from a live tree and annual growth rings counted under a binocular microscope and secondly a tree trunk section from a recently fallen tree was prepared by smoothing and polishing for tree ring counting. These methods showed that the trees were planted between 1835 and 1840, which coincides with historical map evidence of clear cutting and the construction of an artificial lake between 1837-39 to the east of the main catchment. The age of the trees is important as since planting few trees have been felled and the woodland has developed semi-naturally. Survey of standing oaks shows the original planting density was approximately one per $100m^{-2}$ but now there are several clearings where mature trees have fallen. No evidence of the regeneration of oak was seen as few acorns were produced by the senescent trees. The condition of the oak trees was poor, many having dead branches and the majority are stagheaded. Few trees have girths which exceed two metres and the increment core showed evidence of poor growth in many years of the trees life. Other

tree species include Betula pendula (birch), Corylus avellana (hazel), which occur in isolated clumps in the upper catchment and Sambucus nigra (elderberry), Acer pseudoplatanus (sycamore) and Alnus glutinosa (alder), dominate the narrow flood plain and stream banks.

The groundflora is almost entirely represented by Pteridium aquilinum (bracken) except on footpaths and riparian areas where typical woodland species, such as Juncus conglomeratus (common rush), Carex pendula (sedge), Rubus fructicosa (bramble) and Deschampsia flexuosa (wavy hair grass), occur with many other perennial plants, such as Arctium minus (lesser burdock), Galium palustre (marsh bedstraw) and Digitalis purpurea (foxglove). Bracken is dominant under both coniferous and deciduous trees and has dense luxuriant growth reaching frond heights of up to 2.5m, as shown in Figures 2.5 and 2.6 photographed in July when biomass was near maximum.

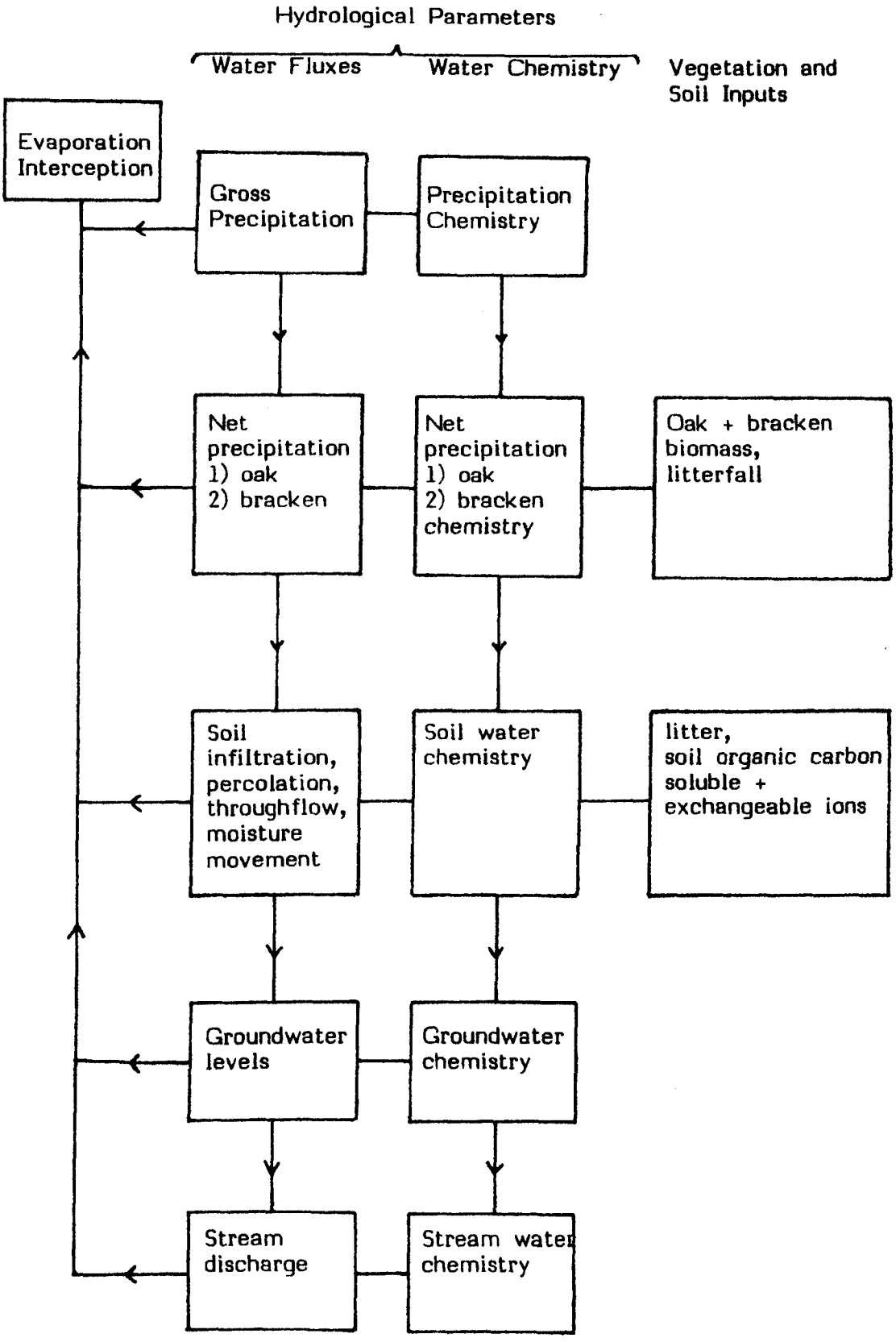
2.2.0 Drainage Basin Instrumentation and Sampling Methodology

An instrumented hillslope section (site 1) was established in September 1978 (Foster and Grieve, 1981) and in September 1979 a stream gauging station and a meteorological station were installed (Figure 2.1). A second instrumented hillslope section (site 2) became operative for this study in June 1980 until December 1981. The experimental framework for site 2 was based on the known fluxes of water through the drainage basin at site 1 and the associated water chemistry, with modifications based on work by Likens et al (1977). Vegetation and soil inputs to the system were incorporated into the framework and Figure 2.7 summarises the experimental framework used. All water samples were collected on a

Figure 2.5 View of hillslope site 2

Figure 2.6 View of hillslope site 2

Figure 2.7 **Experimental Framework**



weekly basis from the catchment when instrument charts were also changed. Soil samples were taken at fortnightly intervals whilst vegetation and the associated soils were sampled at 19 intervals throughout the study period. The following sections describe the instrumentation and sampling procedures devised for this drainage basin study.

2.2.1 **Meteorological Station**

Most field studies require the provision of data concerning local climate since climate is a primary factor determining the occurrence, growth and development of plants and is one of the major soil forming factors (Jenny, 1941). A meteorological station was established at GSP (290977) in an open field on the Merevale Estate, 0.7km from study site 2. Environmental variables monitored were precipitation, temperature and humidity, barometric pressure and windspeed and direction. The site was visited at weekly intervals to collect samples and to change charts on the recording instruments.

i) Gross Precipitation

The problems associated with the accurate and representative measurement of rainfall are well documented, for example, Hayes and Kittredge (1949), Bull (1960), Reigner (1964), Robinson and Rodda (1969) and Green (1970). Problems which influence measured catch include the aerodynamic characteristics of gauges, in and out splash, topography and angle of collection. No absolute standard of precipitation volume exists as no measurement can be made without influencing catch. A variety of gauges have been developed in the past in an attempt to overcome these problems and they are described and evaluated by Gregory and Walling (1973). Standardisation of rainfall gauges

and their installation is essential so that collected data is comparable with other hydrological studies.

Data concerning precipitation volume, intensity, duration and chemistry was required for this study and the first three properties were measured continuously using a Casella^{R} tilting bucket rainfall collector and receiver. The gauge comprised a cylindrical copper container surrounded by a sharp bevelled edge brass ring of 20.32cm (8") diameter linked to a recording device (Figure 2.8B). Rainfall entering the container was funnelled into one side of a copper tilting bucket which tipped and discharged collected water in 0.5mm increments. The empty half of the bucket was then brought up into position and this action closed a circuit causing a pen arm on a drum chart to rise and record the rainfall. A digital counter simultaneously operated so that a cross-check could be made of the chart recordings. Rainfall intensity does affect the accuracy of this gauge type and a correction factor can be used. However, the percentage error for storm intensities experienced in this catchment were sufficiently low that no correction was used. Several other potential sources of error exist with this type of gauge including the diversion of raindrops by wind which could not be avoided and is applicable to all gauge types. The design of the Casella^{R} tilting bucket gauge minimises losses by evaporation and the angled sides of the receiver minimise in and out splash.

The quantity of rainfall to have fallen at any point within the drainage basin was considered to be equivalent to that which had fallen at the meteorological station, although it was appreciated

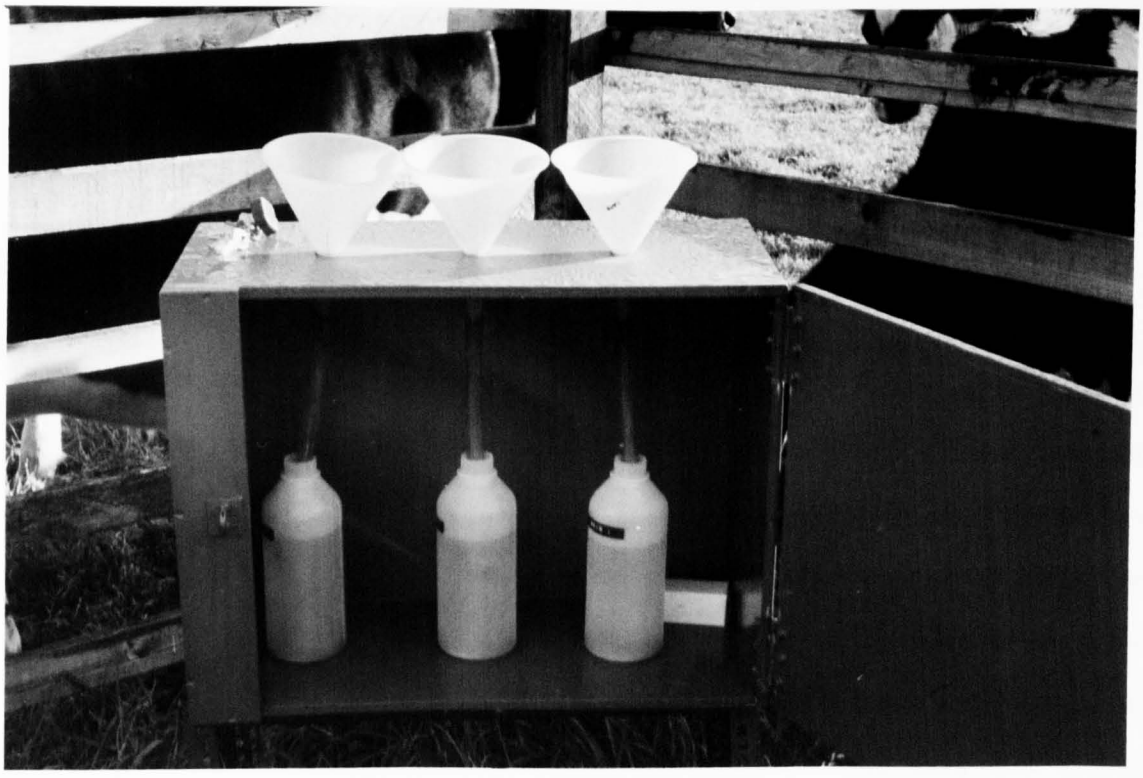


Figure 2.8A Rain gauges

Figure 2.8B Recording instruments

that rainfall characteristics do vary even within a small area (Gregory and Walling, 1973). Snow was only collected in the gauge on two occasions and it was allowed to melt naturally before measurement was recorded thus simulating actual snow melt and hydrological input into the catchment.

Bulk weekly rainfall samples for chemical analysis were collected at the meteorological station using three simple 20cm diameter polythene funnel and bottle gauges supported by a wooden box (Figure 2.8A). Funnels contained glass fibre wool to prevent the entry of contaminants, particularly insects. Volumes were recorded and independently collected samples were analysed initially to identify variability. Variance was very low (4.8%) between the three gauges for all elements and therefore samples were bulked for the remainder of the project. These gauges also served as check gauges for the tilting bucket recorder. This type of collector includes both wet and dry precipitation (Galloway and Likens, 1976) and therefore provides a measurement of bulk precipitation (Likens et al, 1977). Samples were collected from the gauges on a weekly basis and the funnels and bottles cleaned and rinsed with deionised water and the glass wool was replaced each week. It has been suggested that the type of precipitation collector and length of field storage time may affect the chemical quality of rainwater obtained. A recent development of the simple bottle and gauge collector has been the inclusion of ion exchange resins (Crabtree and Trudgill, 1981). Figure 2.9A illustrates the resin collector used in the present study. A comparison of methods and the problems of a sample deterioration over time are discussed more fully in Chapter 3.0.

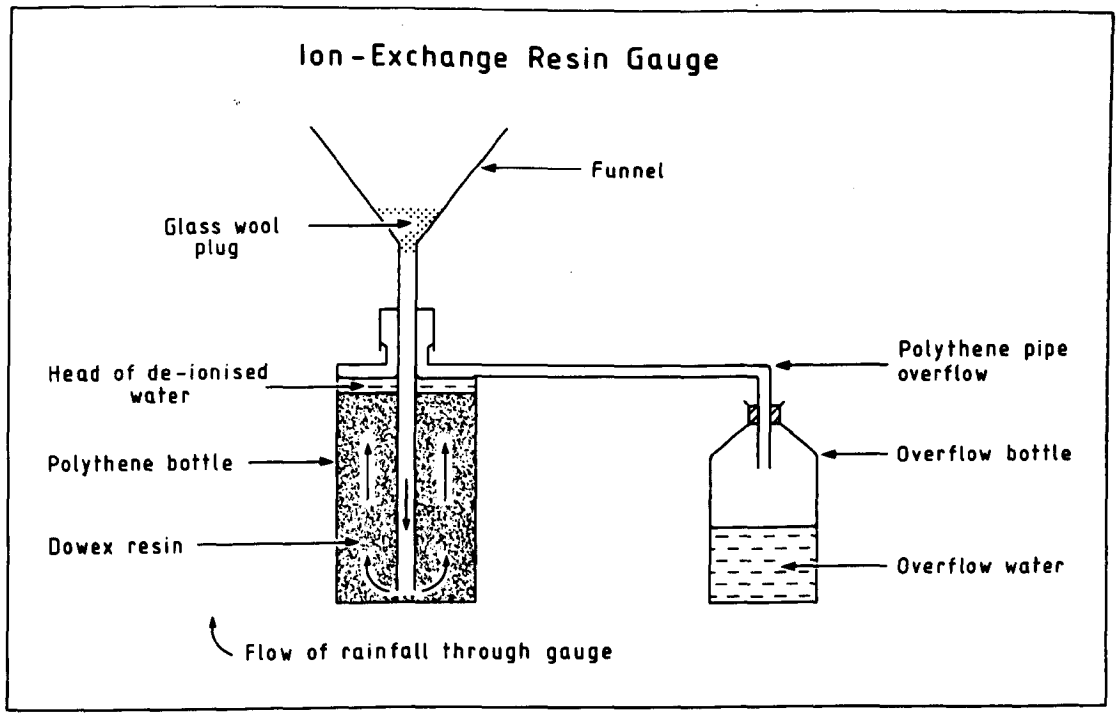


Figure 2.9A

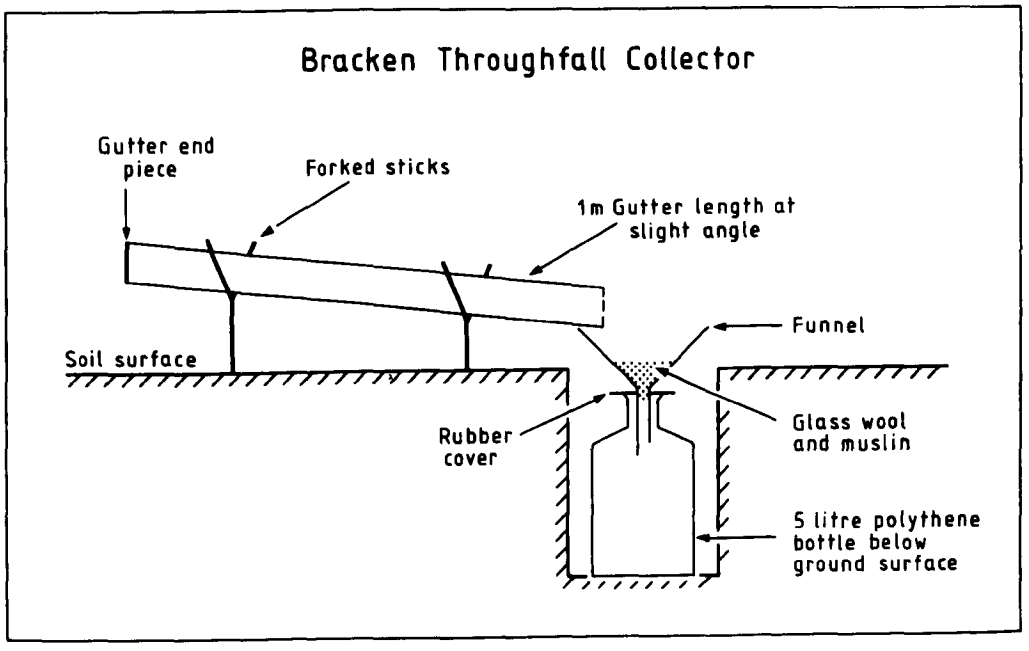


Figure 2.9B

ii) Air Temperature and Relative Humidity

A continuous record of these variables was obtained using a Casella^{R} thermohygrograph located at the meteorological station (Figure 2.8B). Data was recorded on a revolving drum chart but the instrument was not entirely satisfactory due to the non-regulation housing box which moderated extremes of temperature and humidity because of the lack of ventilation. Data was supplemented with information from Birmingham Airport. Figure 2.8B shows the thermohygrograph in the right hand side of the housing box.

iii) Wind Speed and Direction

These meteorological variables were monitored continuously using an automatic weather station - model 1081-87 supplied by Meteorology Research Inc., California. Windspeed was measured by a cup anemometer comprising three 11.43cm diameter conical aluminium cups placed directly above a directional vane allowing simultaneous readings from a single point. Purpose made impression charts provided data in a rectilinear form. This equipment was found to be completely unreliable with expensive repair costs and again supplementary data was obtained from Birmingham Airport.

iv) Barometric Pressure

Continuous records of barometric pressure were obtained using an anaeroid barometer recorder. This instrument provided information for the identification of frontal rainfall and changing air masses.

2.2.2 The Instrumented Hillslope Section (Site 2)

The main study area was approximately 0.1ha in area and consisted of a south-west facing concave hillslope section with a 6^{0} slope and an ephemeral drainage channel at its base. Figures 2.5 and 2.6 show general views across the hillslope whilst Figure 2.10 illustrates the plan and instrumentation of the site. The vegetation of oak trees and bracken understorey are described fully in Chapter 5.0. This hillslope site was selected for detailed investigation as it provided the opportunity for the monitoring of vertical and lateral subsurface water movement, whilst the presence of the ephemeral channel provided an opportunity to monitor surface water chemistry in winter months. The position of this site relative to the stream gauging station is shown in Figure 2.1.

A major problem in intensive studies of this type has been the destruction of the parameters under investigation by continuous sampling and trampling (Ball and Williams, 1978). The study area was therefore divided into two sections, one for instrumentation and the other for sampling of soils and vegetation. The separation of the instrumented and sampling areas prevented mutual interference but allowed comparison due to the proximity of the two sites. Bracken is particularly susceptible to trampling (Watt, 1976) and therefore damage to the study area would be visually identifiable. At the end of the study period only well defined pathways between instruments were evident, the size of the sampling area being sufficient to absorb the impact of investigation.

The following subsections describe the instrumentation and sampling methodology used on the instrumented hillslope.

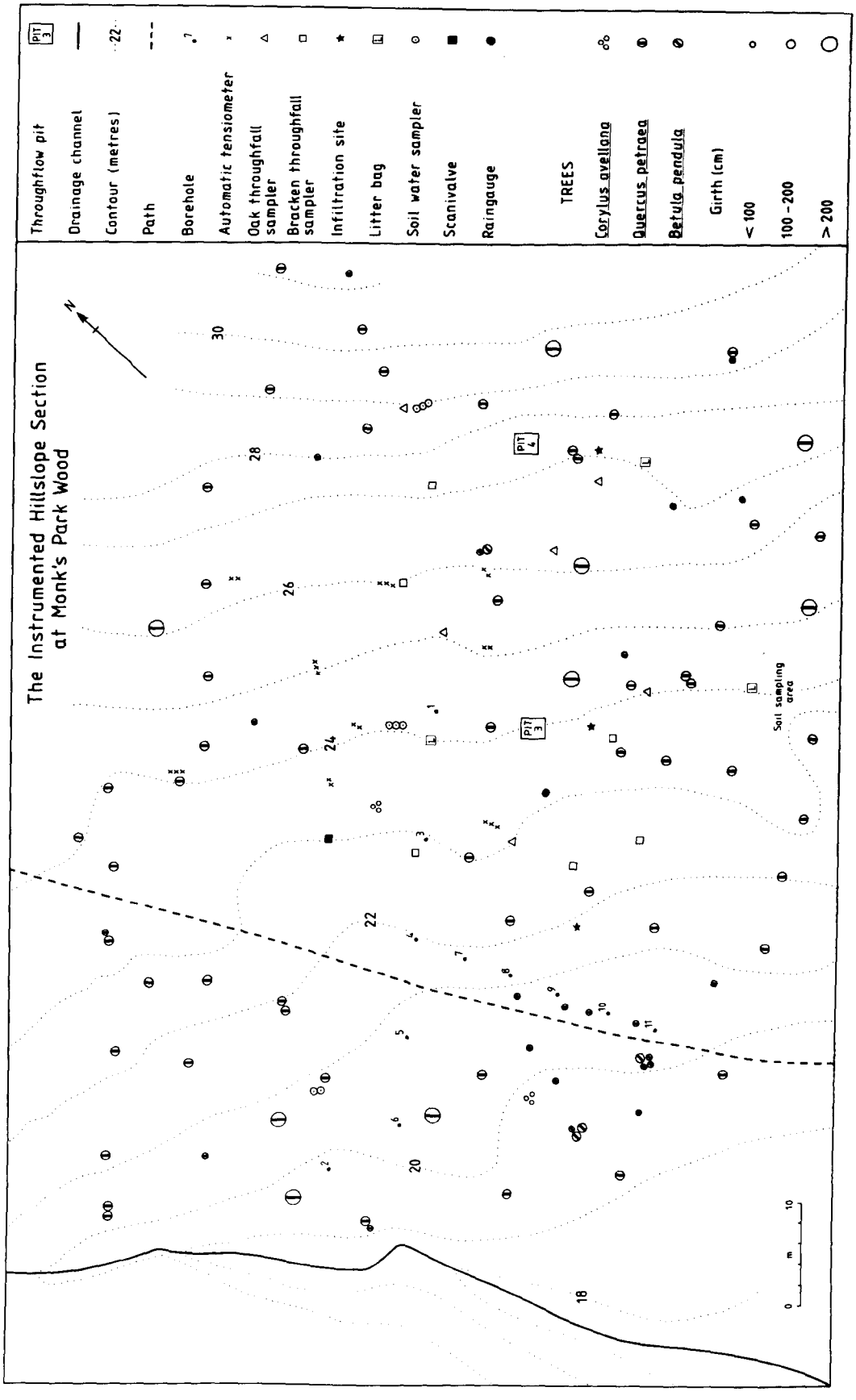

The Instrumented Hillslope Section at Monk's Park Wood
Throughflow pit
Drainage channel
Contour (metres)
Path
Borehole
Automatic tensiometer
Oak throughfall sampler
Bracken throughfall sampler
Infiltration site
Litter bag
Soil water sampler
Scanivalve
Raingauge
TREES
Corylus avellana
Quercus petraea
Betula pendula
Girth (cm)
< 100
100 - 200
> 200
PIT 3
PIT 4
Soil sampling area
N
0
m
10

Figure 2.10

i) Net Precipitation

The problems involved in the collection of gross precipitation were discussed in section 2.2.1.i) and these considerations also apply to the collection of throughfall. However, additional problems are also encountered due to the complex nature of the vegetation canopy. Throughfall is defined as precipitation which drips down through the vegetation canopy, whilst stemflow refers to the precipitation which flows to the ground via the boles or stems of trees or plants respectively. The chemical composition, distribution and quantity of water reaching the ground surface is considerably modified by vegetation type, canopy characteristics and season (Likens et al, 1977) and it is these factors which introduce further complications in the monitoring of net precipitation.

The contribution of stemflow to the amount and timing of net precipitation is related mainly to bark and stem characteristics, (Gersper and Holowaychuck, 1970), the total contribution to net precipitation varying from 1 to 16% for rough and smooth bark types respectively. Carlisle et al (1967) showed that stemflow from Quercus petraea which has a rough, thick, corky bark, accounted for only 2.1% of net precipitation. The relatively minor contribution to net precipitation and the extra collection and analytical work involved did not justify the measurement of this input, although Eaton et al (1973) do note that whilst the volume of water may be small the concentration of some nutrients reaching the ground surface around the tree or plant bole can be significant. Gersper and Holowaychuck (1970) state that in some cases the contribution of nutrients can be so great that soil

chemical properties can be altered, thus partially accounting for soil variability, and identify this 'biohydrologic' phenomena as a soil forming factor.

In this woodland the characteristics of throughfall were affected by the degree of canopy closure, the structure, type and position of fronds and branches and the time of year. Vegetation initially intercepts gross precipitation and a certain amount will be lost by evaporation and absorption, in addition 1 to 3mm of rainfall may be required after a dry perid, to wet a canopy before throughfall occurs (Eaton et al, 1973). The diverse nature of oak and bracken canopies gives rise to a throughfall sample which is heterogeneous in origin and variable in properties across the hillslope. Therefore the type and number of throughfall collectors used for sampling was more critical than that of gross precipitation studies if a representative elementary volume were to be obtained.

Throughfall gauges range from simple bottle and funnel collectors (Eaton et al, 1973) to plastic sheets covering large areas (Calder and Rosier, 1976). Kimmins (1973) found that a wide range of sizes, numbers, densities and arrangements of collectors have been used by other workers but few studies report on the variability of volume and chemical parameters. The trough type gauge used by Leyton et al (1967) has several advantages over the bottle and funnel gauges and plastic sheet collectors. The surface area is adjustable enabling larger collecting areas to traverse a variety of canopy conditions eliminating the need for several funnel gauges, for example, a 10.5cm wide, 1m long trough collects from the

equivalent area of three 20cm diameter funnel gauges (Hayes and Kittredge, 1949). Calder and Rosier (1976) recommend regular irrigation of the soil beneath their plastic sheet collectors and the soil water regime and nutrient dynamics of such irrigated soils will not provide a realistic representation of the true situation. Reigner (1964) evaluated the trough type gauge and found that whilst trough direction had no apparent effect on catch, the angle of slope was important. When raindrops hit a horizontal surface they are deflected vertically and are lost from the collector. Reigner (1964) showed that as the angle of collection increased so did the catch, up to an angle of 25% when actual catch was equivalent to estimated catch. This was because the sloping surface prevented the raindrops bouncing vertically and thus deflected them back into the trough. Raindrop deflection was the main criticism of the trough type gauge by Calder and Rosier (1976) but Reigner (1964) states that a 25% collection angle will minimise any losses. Kimmins (1973) believes that a pilot study should be undertaken prior to the research project to identify spatial and temporal variance of throughfall parameters, but this is only practical if time constraints allow.

The trough type gauge was considered the optimum collecting device for the requirements of this study and the troughs consisted of plastic gutter sections 1.0 x 0.15m providing a collecting area of $1050cm^{-2}$. Six gutters were positioned above the bracken canopy at a height of 1.25m with a 25% slope supported by wooden posts and gutter brackets (Figure 2.11). Throughfall was channelled into a funnel and pipe leading to a 5l bottle. Press-studded elastic straps held the funnel and pipe to

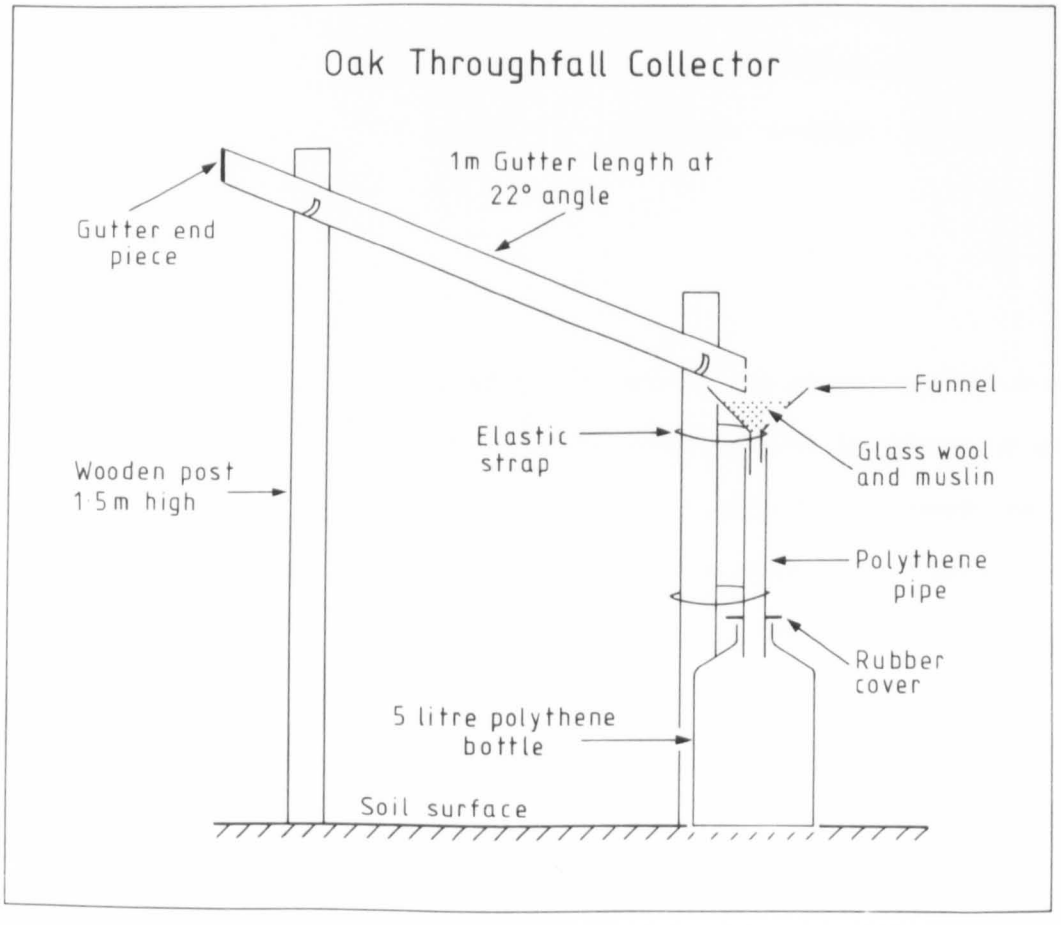

Oak Throughfall Collector
1m Gutter length at 22° angle
Gutter end piece
Funnel
Elastic strap
Glass wool and muslin
Wooden post 1·5m high
Polythene pipe
Rubber cover
5 litre polythene bottle
Soil surface

Figure 2.11

the post and facilitated easy removal for weekly cleaning and the collection of the sample. Six more gutters were placed under the bracken canopy and were angled using forked sticks. Throughfall was channelled via a funnel to a 5l bottle which was installed below the ground surface. Burial of the bottles below the ground surface reduced algal growth and prevented freezing in cold weather (Figure 2.9B). All funnels contained glass wool to act as an inert filter thus preventing the contamination of samples by litter and insects. During the nesting season, these filters were removed by birds and therefore a piece of muslin previously washed in deionised water was placed over the glass wool. It was also found that slugs entered the bottles and therefore rubber covers were made to prevent access. The randomly located and directed positions of the troughs is shown on the hillslope map, Figure 2.10. The 5000m^{-2} instrumented area therefore contained a trough density equivalent to one 20cm funnel gauge per 138m^{-2}. The accuracy of the trough gauges was checked each week by comparison of results with a standard 12.25cm (5") rain gauge which was placed under the vegetation canopy: its position is shown in Figure 2.10.

ii) Infiltration

When gross or net precipitation reaches the ground surface it may lie on the surface but generally, under natural conditions, it seeps into or infiltrates the surface layer and percolates through the soil profile. The aim of infiltration studies is to identify the maximum rate at which water will enter the litter and soil layer over time. The final rate of infiltration approximates to the saturated hydraulic conductivity and the rainfall intensity which

the soil can absorb before surface storage and overland flow occur.

There are three main ways in which infiltration rates can be measured; these are hydrograph separation techniques and sprinkling or flooding infiltrometers. The first method is based on original theories of surface flow (Horton, 1933) and does not account for the more recently investigated phenomena of variable source areas and throughflow (Gregory and Walling, 1973). The second method simulates the action of raindrops from an infiltrometer on a known area and is thought to produce more representative results than the flooding method as it imitates more closely the real event. The flooding method relies on the establishment of a constant head of water on a soil surface. As infiltration takes place the head is maintained by a cylinder of water. Both infiltrometer methods have inherent problems caused by the bounding of a soil area by a containing ring. The insertion of the ring causes disturbance of the soil structure and preferential flow of water may occur down the sides of the ring. The technique aims to measure the vertical flow of water in the soil, but lateral flow can also occur. Gregory and Walling (1973) suggest the use of two concentric containing rings whereby the outer ring is flooded and thus acts as a buffer zone minimising lateral flow from the inner ring. The buffer zone may also have detrimental effects on measurement and therefore Hills (1971) describes a method for correcting results from the use of one cylinder.

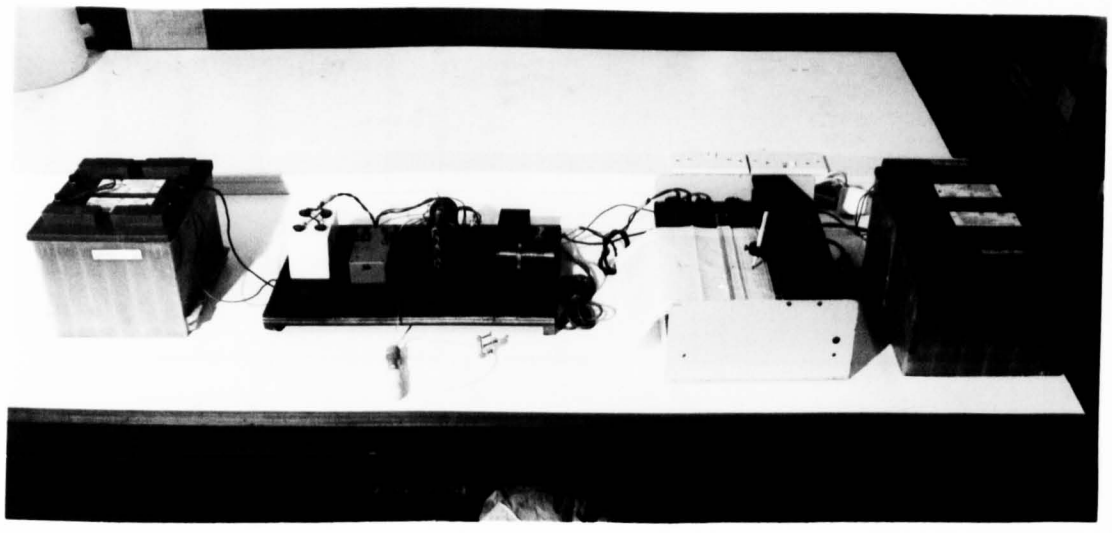
The conventional cylinder infiltrometer described by Hills (1971) consists of an upturned calibrated bottle from which water flows and a constant head is established in a bounded area of the soil. The rate at which water leaves the bottle and therefore enters the soil over time is the infiltration rate. This method has been criticised by Burt (1978a) as being insufficiently sensitive to accurately identify small infiltration rates and suggests an improvement in design by using a calibrated, narrow diameter tube. This would improve accuracy since the surface area is far smaller than that of the Hills cylinder. This new design also facilitates easier operation in the field in that the flow of water from the cylinder can be controlled by clamped tubes and therefore removes the necessity for displacement from the soil area when filling or adjustment is required. A tube infiltrometer was therefore constructed according to the specifications of Burt (1978a) and the equipment was used to measure infiltration rates at three places down the hillslope using a single containing ring (Fig. 2.10). Three measurements were taken at each point in December 1980 and the moisture content of the soil identified. A second series of measurements was taken in June 1981 to identify seasonal differences in infiltration rates. The 15.0cm diameter plastic ring was gently tapped 5cm into the ground and the infiltrometer set up above the ring held by clamps attached to a wooden stake so that the outlet tubes were positioned to provide a constant head of 3.0cm above the ground surface. The amount of water infiltrating the soil was noted every 30 seconds until a constant rate was reached. Volumes were then converted to millimetres and results are discussed in Chapter 4.0.

iii) Soil Moisture and Soil Moisture Potential

The measurement of soil moisture is traditionally performed using the gravimetric technique (Avery and Bascomb, 1982) and the methodology is presented in section 3.2.1. However, the technique is time consuming and destructive and is only recommended for use in long term studies when a calibration measure is required or a soil sample is taken for other analyses, for example, soil samples were required in this study for nutrient analysis and therefore gravimetric determinations were also made. Alternative methods are available for the indirect measurement of soil moisture and require initial calibration with gravimetric samples. These methods include the use of neutron probes, soil psychrometers, gypsum blocks and tensiometry (Gregory and Walling, 1973). This study required the identification of soil water status and the movement of water within the hillslope section on a continuous basis. Tensiometry provides a measure of soil moisture suction in a soil and this information enables calculation of soil moisture content when a soil moisture suction curve has been established. Soil water movement can also be identified as moisture fluxes which occur in response to soil water potential gradients. A water filled ceramic porous cup is placed in the soil at a required depth and changes in soil moisture content are identified by the flow of water in and out of the cup causing changes in tension to be translated to a gauge or recording device.

Burt (1978b) describes a system whereby soil moisture potential can be monitored on a continuous basis using a Scanivalve^{R} automatic tensiometer system. A network of tensiometers linked

to a central recording device provides a continuous measurement of soil moisture potential over a given area and thus provides information suitable for the calculation of continuous soil moisture records and the identification of lateral and vertical flow pathways. The system is based on a scanning fluid wafer switch which has the advantage of a stepper drive motor which enables more than one tensiometer to be linked to a single pressure transducer. A total of 24 tensiometers can be used with two acting as reference points. Figure 2.12 illustrates the system used in this project. Tensiometers were constructed from ceramic porous cups obtained from Soil Moisture Equipment Corporation (Appendix I) size 2.75cm length, 2.0cm internal diameter with a 1.23cm neck length and 1.3cm neck diameter. A 6.0cm length of heavy duty polythene tube with a 1.2 cm internal diameter was attached to each cup by first heating to expand the tube and then glueing into place with Araldite^{R} to provide a water and airtight seal. A rubber bung with two drilled holes was placed in the top of the tube and then PVC tubing with 2.5mm internal diameter and a 0.5mm wall was glued into both holes as shown in Figure 2.12, one acting as the connection to the fluid wafer switch and the other as a bleed tube. Nylon tubing with 1.5mm outside diameter was obtained from the Scanivalve Company (Appendix I) to attach to the inlet tubes of the scanning switch. These tubes were joined to the PVC tubing from the tensiometer through a connection block consisting of a piece of hardboard through which the tubes are passed and joined together using Araldite. Two inlets are reserved for zero and 100cm tension reference points and these tubes are not attached to a tensiometer, but are placed inside a



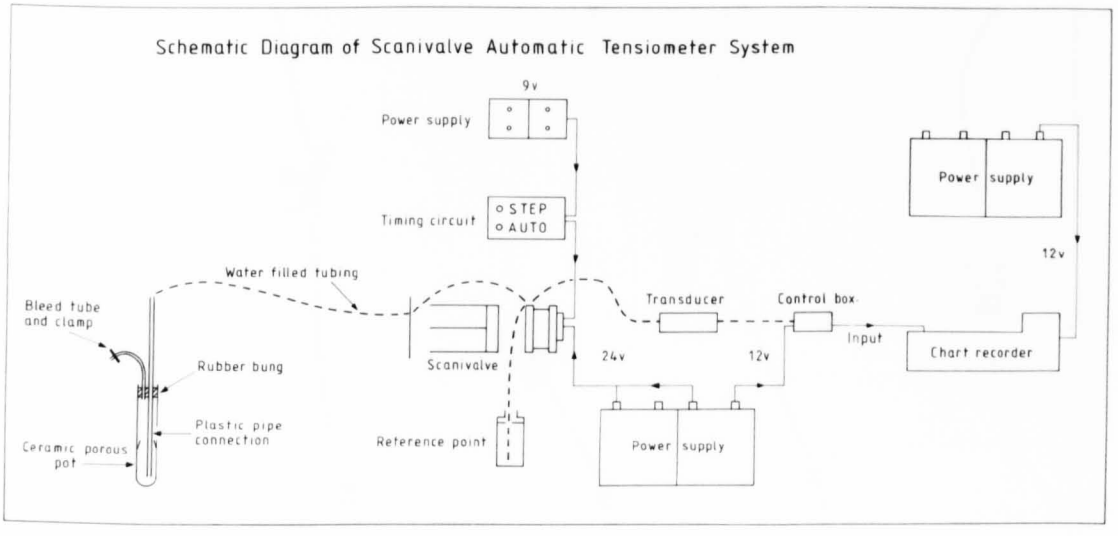
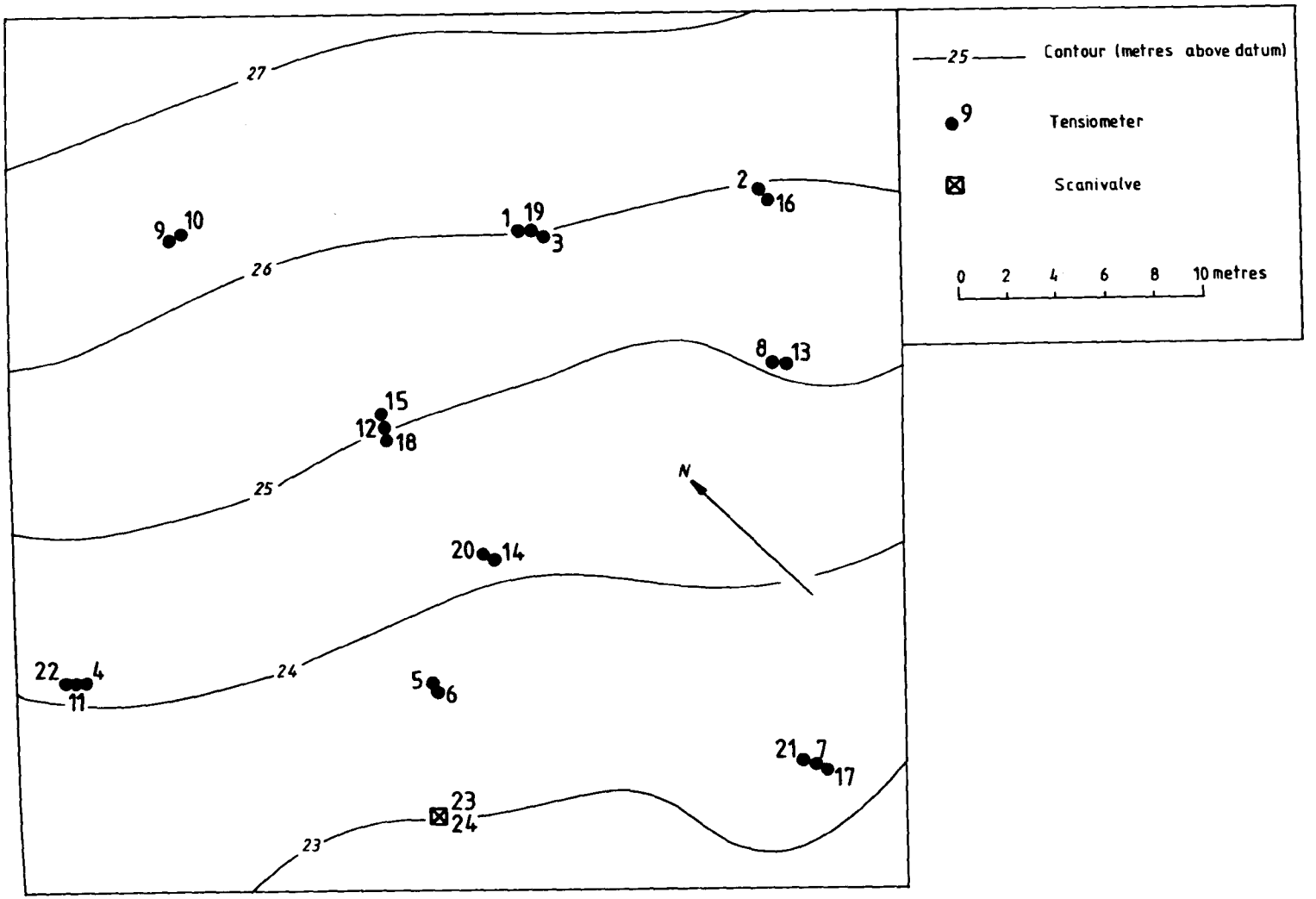


Figure 2.12 Tensiometer system

Detail of Tensiometer Grid



container of water open to atmospheric pressure. The fluid scanning switch and stepper drive motor are supplied together and were mounted on a wooden block and the nylon tubings attached to the inlets. The pressure transducer (Pressure Sensors Ltd, Appendix I) with a $100^{\pm}$MV range was connected to the Scanivalve outlet using the same tubing arrangement as the tensiometer connections. The transducer was connected to a control box which directs the necessary 12 volt supply to the sensor and receives the electrical output from the transducer. The output was recorded on a JJ Instrument^{R} flat bed chart recorder CR550B from Educational Measurements Ltd (Appendix I), which had a battery option. Z-fold paper was used for recording as this facilitated easier examination of the data than the normal chart rolls. The Scanivalve stepper drive motor was operated using an electronic timing circuit constructed using a circuit suggested by Burt (1978b), which advances the motor at an interval of approximately 2.5 minutes. This enables a full cycle of tension readings to be obtained in one hour. The response time for the pressure transducer was found to be only a few seconds and this time interval was sufficient for output stabilisation. The circuit was powered by two 9 volt rechargeable batteries and provided start and autohome switches which enable one advancement of the stepper motor or return to the zero reference outlet respectively, which greatly aided filling and bleeding of the system.

The system was filled with deaerated water as described by Burt (1978b) using a car foot pump to provide a pressurised supply of water from a large bottle into the tensiometer tubes. Eventually the tensiometer system would fail due to air perpetrating the

apparatus via the tensiometers and the equipment had to be bled. This was only necessary every 12 weeks.

The system can operate from a mains supply but as this was not available rechargeable batteries were used. The chart recorder was powered by two 12 volt car batteries of 47 amp hours and the Scanivalve by 24 volts supplied by two 12 volt car batteries in series. The pressure transducer was powered by 12 volts from one of these batteries. The main constraint on the use of this system is battery consumption. Eight car batteries are required in total, including charged replacements, to operate a single system. The chart recorder is the main consumer with battery replacement occurring twice weekly, whilst the Scanivalve batteries were replaced every four weeks. The power supply in this project was provided by heavy duty 12 volt car batteries loaned by Lucas Batteries Ltd with the kind co-operation of Mr J Ponsford and Mr K Owen. The system was initially housed in wooden boxes but recurrent vandalism and theft of batteries caused considerable loss of data and damage. Therefore, galvanised steel boxes with hardened steel hasps and padlocks were purchased from Arbury Engineering Ltd (Appendix I) and were attached to concrete slabs and partially buried at the site. The Scanivalve, transducer and timing circuit were mounted together on a wooden block with detachable electrical connections facilitating easy removal for repair and maintenance.

The tensiometers were installed at three depths over the hillslope, namely, 15, 30 and 70cm depths which corresponded with the Ah, Bt(g) and BCg soil horizons respectively. A hole was augered

using a 3.5cm diameter cylindrical corer and the tensiometer lowered to the required depth with the bleed tube remaining at the soil surface. The hole was backfilled with a slurry of excavated soil to provide good hydraulic contact between the ceramic pot and the soil. The position of each pot was marked using a numbered 2m garden cane and all tubes were buried below the litter layer. The exact position of each tensiometer in terms of depth and location on the hillslope were identified by levelling and plane table surveying and their positions are shown in Figure 2.10, 2.12. Extreme accuracy is required in levelling as a small error can introduce large discrepancies in the calculated soil moisture potential.

The calculation of soil moisture potential from the recorded output was performed using a purpose written program for a PET microcomputer (I.D.L. Foster, Coventry Polytechnic). The relative height of each tensiometer above the transducer must be identified and the matric potential or positive pressure of the soil was calculated thus:

$$P - H = T \quad \text{(Burt, 1978b)}$$

where P = record pressure

H = height above or below transducer

T = calculated matric potential or positive pressure

The pressure transducer was calibrated before use in the field to establish the relationship between soil moisture potential and output voltage. The relationship was found to be linear and

consequently enabled input to the microcomputer directly from the recorded trace.

iv) Soil Water

Water which enters the soil matrix is held under tension by capillary forces and soils which are above field capacity will also possess gravitational water. Gravitational water percolates freely through the soil profile and therefore soil water samples can only be obtained when the soil is saturated. In reality most soils are below field capacity for most of the year and a sample of soil water for chemical analysis must be obtained by applying a suction equal or greater than that of capillary tension. Wagner (1962) described a system for obtaining a soil water sample from the unsaturated zone of a soil profile using a suction or vacuum lysimeter. Since this time various modifications have been introduced, Parizek and Lane (1970), Wood (1973) and Duke and Haise (1973) but the instrumentation remains fundamentally the same and consists of a porous ceramic pot and pipe assembly embedded within a soil profile to which a vacuum is applied. Soil water is drawn into the pot and can be evacuated into a collection flask using a vacuum pump. At present this is the only practical method available for obtaining a simple direct sample of soil water in the unsaturated zone. The methodology and field operation has been severely criticised by England (1974) who voices serious doubts about the representativeness of such water samples and Hansen and Harris (1975) question the validity of the method believing there to be substantial bias and variability involved in the use of this sampling method. England (1974) notes that water will be drawn from a variety of pore sizes which

will consequently affect nutrient concentrations, for example the distribution of cations will vary according to the degree of association with the negatively charged soil particles from the surface of electronegative colloids and soil particles. Therefore soil water from a macropore may be of different chemical quality to water obtained from micropores. Chemical concentration will also depend on soil moisture content, hydraulic conductivity, the amount of suction applied and pore size distribution around the sampling cup. Hansen and Harris (1975) add that solute concentration is affected by cup size, rate of inflow and the incoming solute concentrations. They also note that significantly different concentrations are obtained depending on the initial sampling vacuum.

Problems arise with porous cups themselves which may contain contaminants - washing in dilute hydrochloric acid has revealed concentrations of a few mg l^{-1} of sodium, calcium, magnesium, bicarbonate and silica. The ceramic cup has its own exchange capacity and may absorb significant quantities of nutrients, for example Hansen and Harris (1975) found up to 110 ug of phosphorus was absorbed by a single cup. However, they believe absorption only to be a problem when the exchange capacity of the cup exceeds that of the surrounding soil. On installation the continuous drawing in of water and suspended sediments can 'screen' the cups reducing their efficiency and biasing the chemical content of soil water. Hansen and Harris (1975) found that a 60% decrease in efficiency can occur in one year. Parizek and Lane (1970) prevented this happening by embedding their lysimeters in a cushion of crushed pure silica sealed with a

layer of bentonite clay (both have negligible exchange properties) and this provided a clear transmission medium from soil to lysimeter preventing organic matter, soil particles and colloids clogging up the ceramic cup. The installation also provided good hydraulic contact, filled uneven soil voids and prevented the drainage of water from the surface down the lysimeter. Wood (1973) believes that these seating materials can affect the chemical quality of surrounding soil and the traversing soil water and he recommended backfilling the installation with sieved excavated soil providing a more natural contact. He used a 1 bar porous cup which did not clog up readily and did not cause excessive filtration of the solution.

Other methods of obtaining soil water from the unsaturated zone include the use of pan lysimeters (Parizek and Lane, 1970), vacuum trough extractors (Duke and Haise, 1973) and the Ebermayer Lysimeter (Jordan, 1968). All operate on the principle that the overlying soil remains undisturbed which is achieved by installation of the lysimeter into the side wall of a pit. Installation and instrumentation are complicated and the increased cost was restrictive to this study and the many problems involved with suction lysimeters are also applicable to these other methods. Consequently vacuum lysimeters were constructed based on the design of Parizek and Lane (1970) consisting of a 1 bar ceramic porous cup attached to a 1m length of PVC drainpipe and collar and sealed with Araldite (Figure 2.13, 2.14B). The top of the pipe was sealed with a rubber bung which had two access points consisting of glass tubes enclosed in rubber pipe and sealed with Araldite. One tube was extended with 2mm I.D. polythene tubing

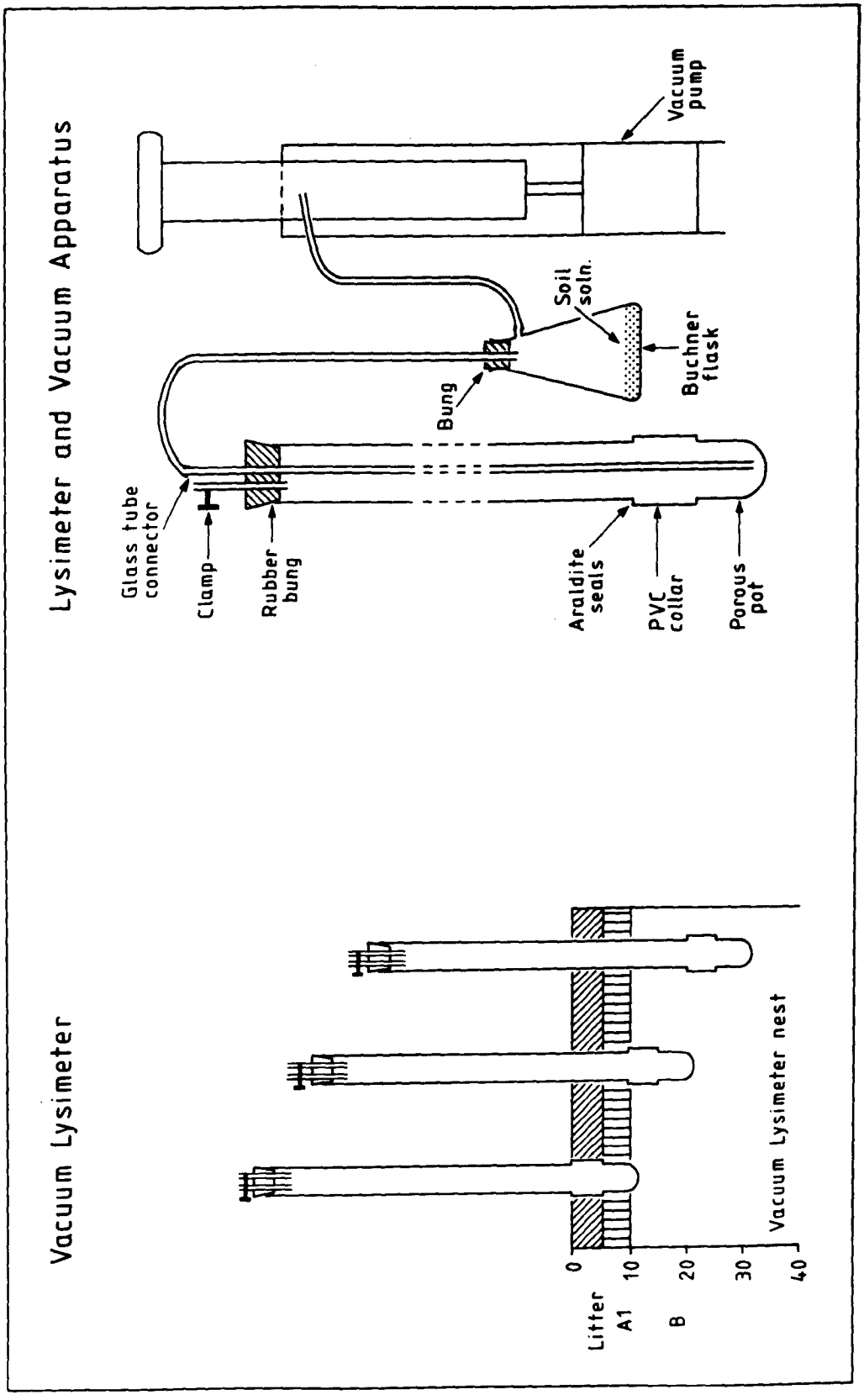

Lysimeter and Vacuum Apparatus
Vacuum pump
Soil soln.
Buchner flask
Bung
Glass tube connector
Clamp
Rubber bung
Araldite seals
PVC collar
Porous pot
Vacuum Lysimeter
Vacuum Lysimeter nest
Litter
A1
B
0
10
20
30
40

Figure 2.13

Figure 2.14

Figure 2.14A Cylindrical corer

Figure 2.14B Lysimeters in the field

to reach the base of the ceramic cup, for sample evacuation and the other tube allowed pressurisation of the system. The lysimeters were installed in nests of three at 10, 25 and 35cm depths in the soil profile at three locations down the hillslope (Figure 2.10). Holes were augered to the relevant depth and backfilled with a slurry of excavated material to ensure good hydraulic contact. Samples were evacuated using a hand operated vacuum pump and sealed with screw clamps. It was not possible to use a constant vacuum apparatus recommended by Hansen and Harris (1975) and the vacuum was allowed to fall over one week when the water sample was removed by releasing the clamp and attaching a rubber tube to the evacuation line and applying a suction from the pump. Soil water was drawn up into a Buchner flask as illustrated in Figure 2.13. When the soil solution had been removed, the second tube was clamped and the vacuum replaced.

Soil water which moves downslope in the unsaturated zone can be intercepted using throughflow pits which consist of an exposed vertical soil face to which troughs are attached at strategic positions to collect water flowing through different horizons. The interception of such water allows a determination of chemical composition and enables an estimate of the amount of subsurface flow occurring over time to be calculated. Throughflow pits have been used in many investigations, for example Whipkey (1965) and Dunne and Black (1970); the different types of pit are very similar though the size of the exposed soil face varies from 1m to 85m. This large range is due to the severe problems which are

encountered when calculating the contributing area of the sample obtained. The very presence of the pit distorts the natural flow pattern of water within the soil and thus the soil hydrograph is altered. Knapp (1973) states that the contributing upslope width is rarely the same as pit width and throughflow volumes must be corrected for this. He placed the tensiometers around throughflow pits and from plots of the resulting potentials and flow nets it was found that when the soil was dry unsaturated throughflow was directed on either side of the pit towards the free face. When saturated throughflow occurred soil water moved away from the free face. Thus in the latter case the contributing area to the throughflow sample will be considerably decreased. Atkinson (1978) states that if budgets are to be calculated then this important phenomena must be taken into account and values corrected using tensiometers. The second problem associated with the presence of the pit is that the sample collected will consist only of saturated throughflow. For water to leave the exposed face, water must be at atmospheric pressure, otherwise it will be retained in the soil, consequently a dynamic saturated wedge builds up behind the exposed face which additionally distorts the flow of soil water. Naturally occurring saturated wedges, such as those on stream banks are more suitable for intercepting throughflow as artificial conditions are not created (Atkinson, 1978). Very large variations have been found in the quantity and quality of throughflow occurring between catchments and even within the same study plot. Whipkey and Kirkby (1978) suggest topography, vegetation, soil type and structure can greatly influence volumes, for example, the presence of enlarged pores or cracks in the exposed face will increase

volumes intercepted. Artificial boundaries inserted upslope of pits have been employed so that the contributing area is defined. Whipkey and Kirkby (1978) believe that these barriers may encourage preferential flow and do not recommend them.

The amount of subsurface flow occurring may be estimated from the increase in discharge downstream and therefore several gauging points within a catchment would be required, but no direct information on chemical quality would be obtained. Recent developments in the use of ion exchange resins to monitor nutrient fluxes have been made with the supposition that the chemical quality of throughflow can be more accurately estimated by emplacing such resins in the soil and eliminating many of the interfering effects of throughflow pits. The information obtained is supplemented with tension and throughflow volumetric data so that solute budgets can be calculated. The use of these resins is still in the experimental stage and data on their effectiveness not readily available. Furthermore the extraction of ions from the exchange resin (Section 3.5.0.ii)) is laborious and subject to dilution errors. As the resin technique was not suitable for a weekly monitoring scheme the pit method was used in this investigation and Figure 2.10 shows the locations of two 1m face pits. Soil was excavated to approximately 1.5m depth in both pits. Knapp (1973) states that the pits should ideally be excavated to bedrock but this was not possible in this study due to the thickness of the underlying drift deposits. Plastic sheets were inserted into the A, B and BC soil horizons using a flat blunt knife which removed the need to excavate and disturb sections of the soil. Each sheet was attached to a slightly

sloping 1m length of guttering and held in position by a dexion framework. Throughflow was then directed into collection bottles via 8.0cm funnels with glass wool filters (Figure 2.15).

The pits were covered with a varnished marine plywood and hinged and padlocked to a piece of embedded dexion. Throughflow troughs were also installed on the banks of the drainage channel to collect water flowing through the A horizon. These troughs were covered by polythene sheeting to prevent the entry of rainwater.

The pathways which soil water follows both within the unsaturated and saturated zones can be monitored using tracers. Radioactive tracers have been used (Atkinson, 1978) such as Iodine ^{131}I and Tritium ^{3}H, but these tracers require specialist laboratory equipment and can occur "semi-naturally" in an ecosystem; for example, Tritium is a product of nuclear fallout and its presence may interfere with results. Clarke (1981) used insoluble disperse dyestuffs to identify shear planes, as an inherent property of the dye used was to lodge onto rough surfaces of soil. Bouma et al (1977) and Bouma et al (1979) used methylene blue to identify preferential flow through soil macropores, but the most common tracer used in hydrological studies is the fluorescent dye. Reynolds (1966) recommended the use of the fluorescent dye, Pyranine, to identify the vertical movement of soil water in a woodland and Trudgill et al (1980) used Lissamine FF to calculate soil water residence times. Fluorescent dyes have also been used to identify pipe and groundwater flows especially in Karst topography (Drew and Smith, 1969). Smart and Laidlaw (1977)

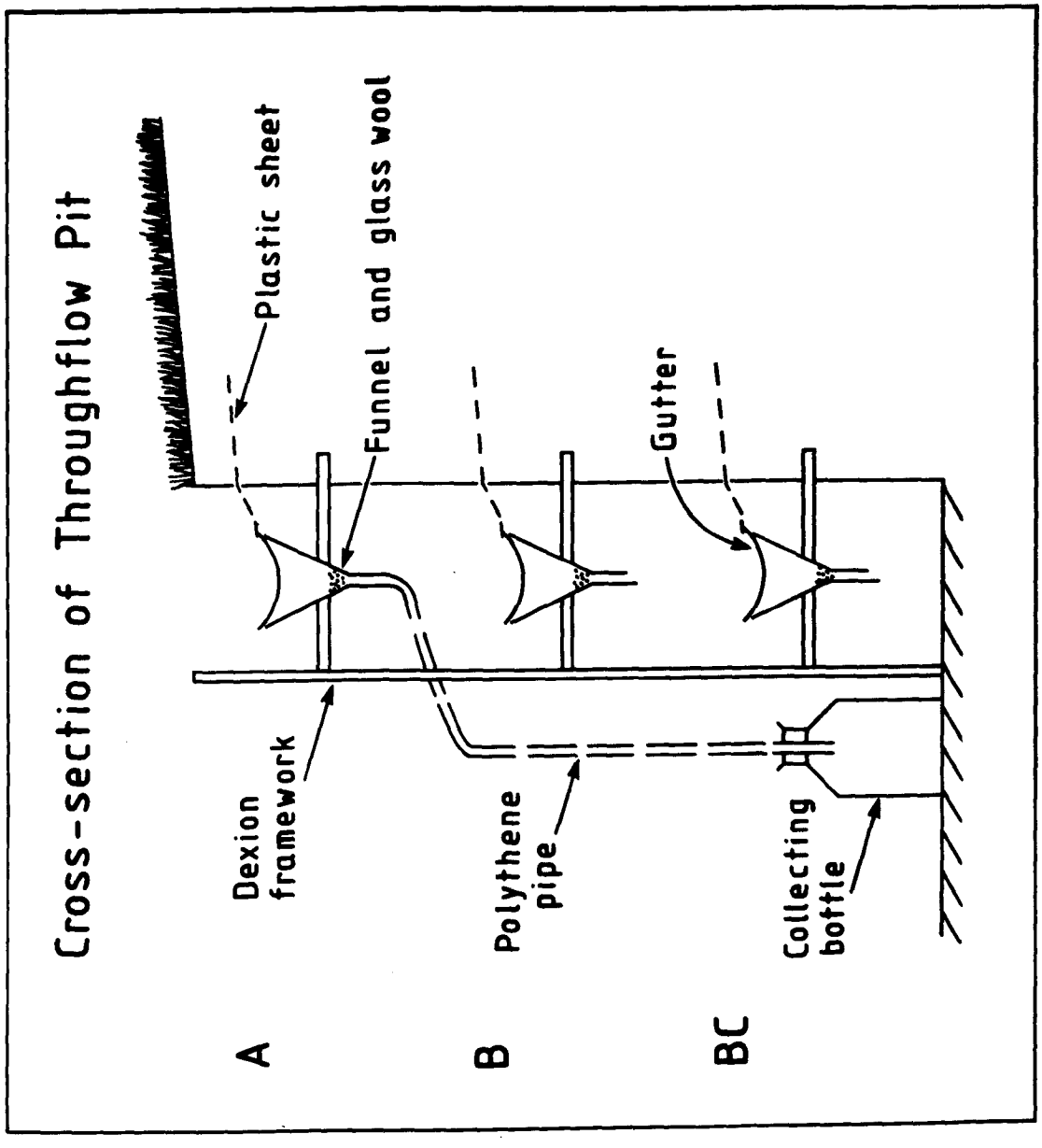

Cross-section of Throughflow Pit
Plastic sheet
Funnel and glass wool
Gutter
Dexion framework
Polythene pipe
Collecting bottle
A
B
BC

Figure 2.15

provide a comprehensive review of most aspects of fluorescent dye tracing and evaluate eight different dyes. The recovery of a dye after application is dependent on many factors including dilution, adsorption, photochemical and chemical decay, biodegradation and temperature. These factors are most critical when dye tracing is being used to calculate discharge rates but the aim of this experiment was to simply identify pathways.

The choice of dye was therefore controlled by recoverability in a woodland environment with high levels of organic matter. Smart and Laidlaw (1977) recommend the use of an anionic green dye, Lissamine FF, as it is extremely stable and not prone to adsorption. Sulpho-rhodamine B, an anionic orange fluorescing dye, required only a very small initial quantity for detectable fluoresence. Both dyes have sulphuric acid functional groups which together with their negative charges minimises adsorpiton by organic matter. Samples of these dyes and advice on their use in the field were obtained from Sheffield University, Department of Geography.

Quantities of dye were placed in the field on 30 9 81 when the soil moisture deficit began to be replenished and groundwater levels were rising. Information was required on the flow pathways of infiltrating water and this was obtained by placing 5g of Lissamine FF on the litter surface in each of three 1m squares located down the hillslope. After five weeks when approximately 50mm of throughfall had occurred and potential evapotranspiration was minimal, soil cores were taken from each square at 5cm intervals up to 60cm depth. A trench was then excavated to observe the exposed soil face in each square.

The percolation rate of soil water was investigated using the midslope suction lysimeters. 5g of Lissamine FF was sprinkled on the litter surface around each of the three lysimeters which were sampling at 10, 20 and 35cm depths. No dye was placed next to the drain pipe as preferential flow down the pipe may have occurred. When the lysimeters were evacuated in following weeks samples were tested for the dye.

A 0.3 x 1.0m band of Lissamine FF was placed on the litter surface 1m upslope of each of the throughflow pits. Sulphorhodamine B was placed under the litter layer to minimise adsorption effects by the litter and subsequent throughflow samples analysed for both dyes.

The pathways of saturated flow were followed by injecting a 5g sample of Lissamine FF into a natural water filled depression in the ground created by an uprooted tree at a point between the Scanivalve control boxes and the footpath (Figure 2.10). Five more small boreholes (Nos. 7-11) were constructed downslope from the injection site, roughly parallel to the footpath. A small water sample from each hole was taken at weekly intervals for dye detection using a McCartney bottle which was lowered into the hole on a piece of string. A 5g sample of Lissamine FF was also placed in Borehole No.2 nearest to the drainage channel. Any subsequent channel flow was then tested for the presence of the dye.

v) Groundwater

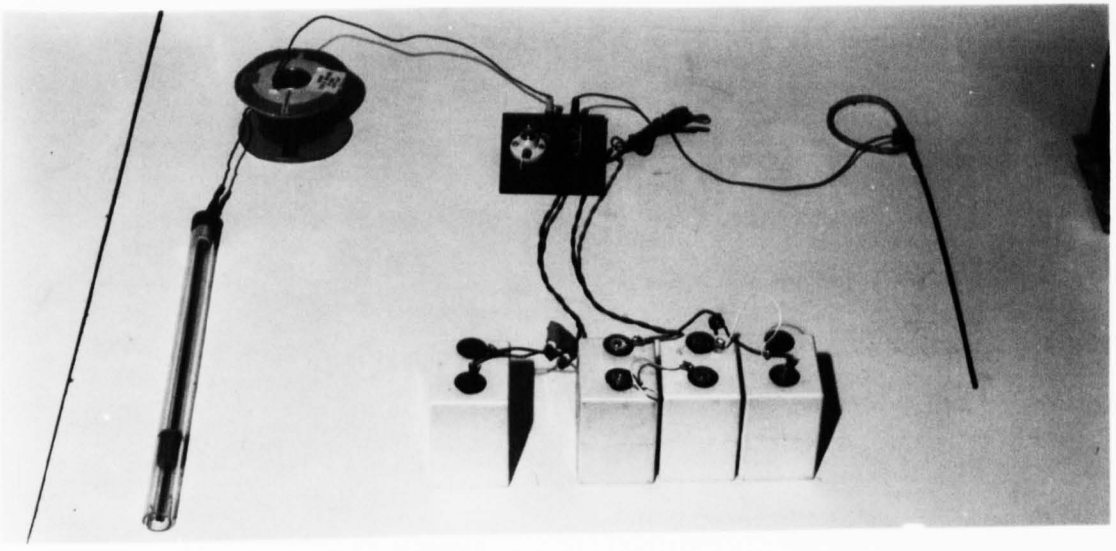
Groundwater levels are controlled by the amount of percolation and evaporation which occurs within the drainage basin. The changing levels which occur in response to rainfall events and season can be monitored using borehole installations. Robson and Thomasson (1977) recommend the construction of 10cm diameter wells using a Jarratt or similar auger. The time of installation can be critical because excavation during wet months may cause smearing which seals natural cracks and pores thus creating unreliable water levels. If the soil structure is poor the borehole may need to be supported with a porous pipe or slotted plastic pipe. A cover is also necessary to prevent animal interference and the entry of rain. Gregory and Walling (1973) recommend backfilling the borehole around lining pipes with gravel so that good hydraulic contact is made. The borehole water level represents the depth of the groundwater table below the soil surface, that is, the upper level of the saturated zone; however, Robson and Thomasson (1977) state that if a soil has a low percentage of coarse pores the water level may remain artificially high when the soil is drying out; such a well needs to be artificially drained and should then reach its optimum level.

Manual and recording devices are available for monitoring water levels, with the depth from ground surface normally measured using a steel tape, electronic contact device or a float system. Equipment was not available for the continuous monitoring of groundwater levels and therefore two observation boreholes of 10cm diameter (No.1 and 2, Figure 2.10) were excavated in October 1980 to a 3m depth using a Jarratt auger. The sides of

the boreholes were not lined and marine plywood lids were placed over the holes. In March 1981 further boreholes were excavated downslope (Nos.3-6) using a 3.5cm diameter cylindrical corer (Figure 2.14A) to 60cm depth. These small holes remained, without maintenance, to the end of the study period.

The water levels were initially monitored using a steel tape but difficulty was experienced in detecting the correct level. An electrical contact device was therefore constructed (Figure 2.16) consisting of a brass contact rod which was placed in the soil and a second rod encased and supported in a 2cm diameter perspex tube with rubber corks. Water is too weak an electrolyte to carry the current necessary to complete the circuit and therefore a relay was incorporated into the circuitry which reinforces the weak current over a distance with a local battery. When the probe reached the water surface the light bulb was illuminated and the appropriate length of wire to the probe was then measured. The relay was powered by a 27 volt supply from three rechargeable 9 volt batteries and the light bulb powered by a separate 9 volt battery. The batteries and circuit board were then placed in a plastic card index box with drilled holes for the wire and light bulb connections so that the equipment was waterproof in the field.

Samples of groundwater for chemical analysis were obtained from borehole No.1 at weekly intervals by lowering a weighted bottle on a length of string into the borehole.



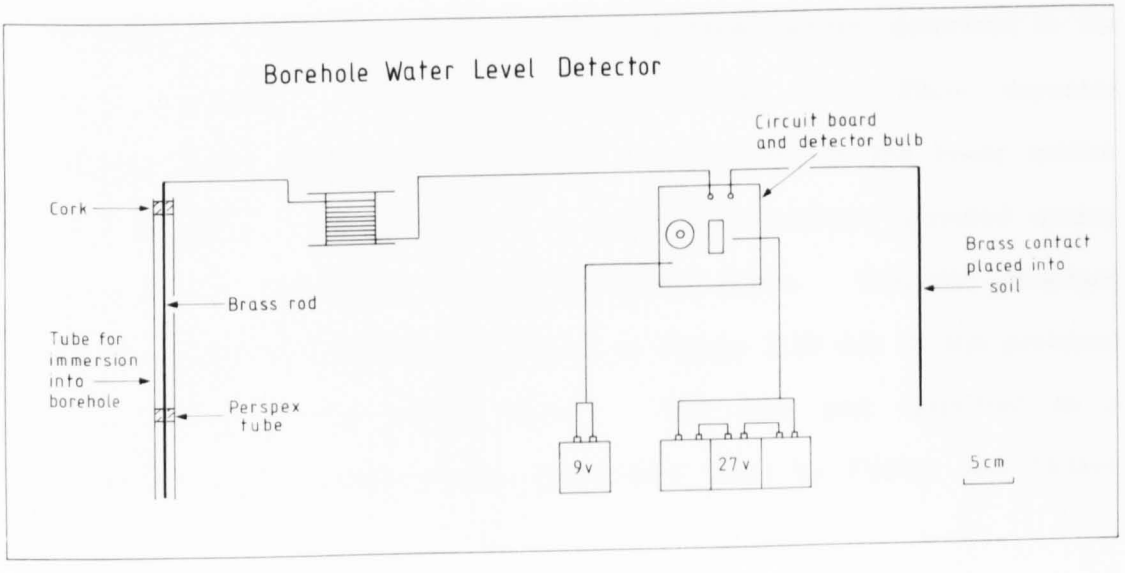

Borehole Water Level Detector
Circuit board
and detector bulb
Cork
Brass rod
Tube for
immersion
into
borehole
Perspex
tube
Brass contact
placed into
soil
9v
27v
5cm

Figure 2.16

2.2.3 The Instrumented Hillslope Section Site 1 and Streamflow

Site 1 was established in December 1978 and formed the initial experimental site of a now larger investigation (Dearing et al 1982). A detailed map of the site (Figure 2.17) shows its characteristics and instrumentation. The site consisted of a small 20^{o} hillslope hollow adjacent to the main stream of the drainage basin and was fairly representative of the main soil and vegetation identified in the catchment (Foster and Grieve, 1981). The data obtained for this hillslope section was available for supplementation, comparison and confirmation of results from Site 2.

Instrumentation was very similar to Site 2 with the use of suction lysimeters, two throughflow pits and manual tensiometers, described in the previous sections. Throughfall was collected using 20cm diameter polythene funnel gauges and a borehole was installed on the lower section of the hillslope. Two Casella ^{R} L Earth thermometers provided weekly records of soil temperatures at 4.0 and 8.0cm depth. This site possessed a wider variety of vegetation as shown in Figure 2.18 due to the presence of the floodplain and stream bank. Soil type was classified as a stagnogleyic brown earth (sandy loam over clay) by Foster and Grieve (1981).

Flow records for the main stream were obtained using a Munro ^{R} vertical drum stage recorder linked to a compound V notch weir. This instrument's design is based on a float and counterweight system installed in a stilling well which prevents turbulence and stream currents influencing the recording. The instrument was positioned on the stream bank and connected to the stream water by a 5.0cm diameter drain pipe. The water in the stilling well remained at the same level as the stream,

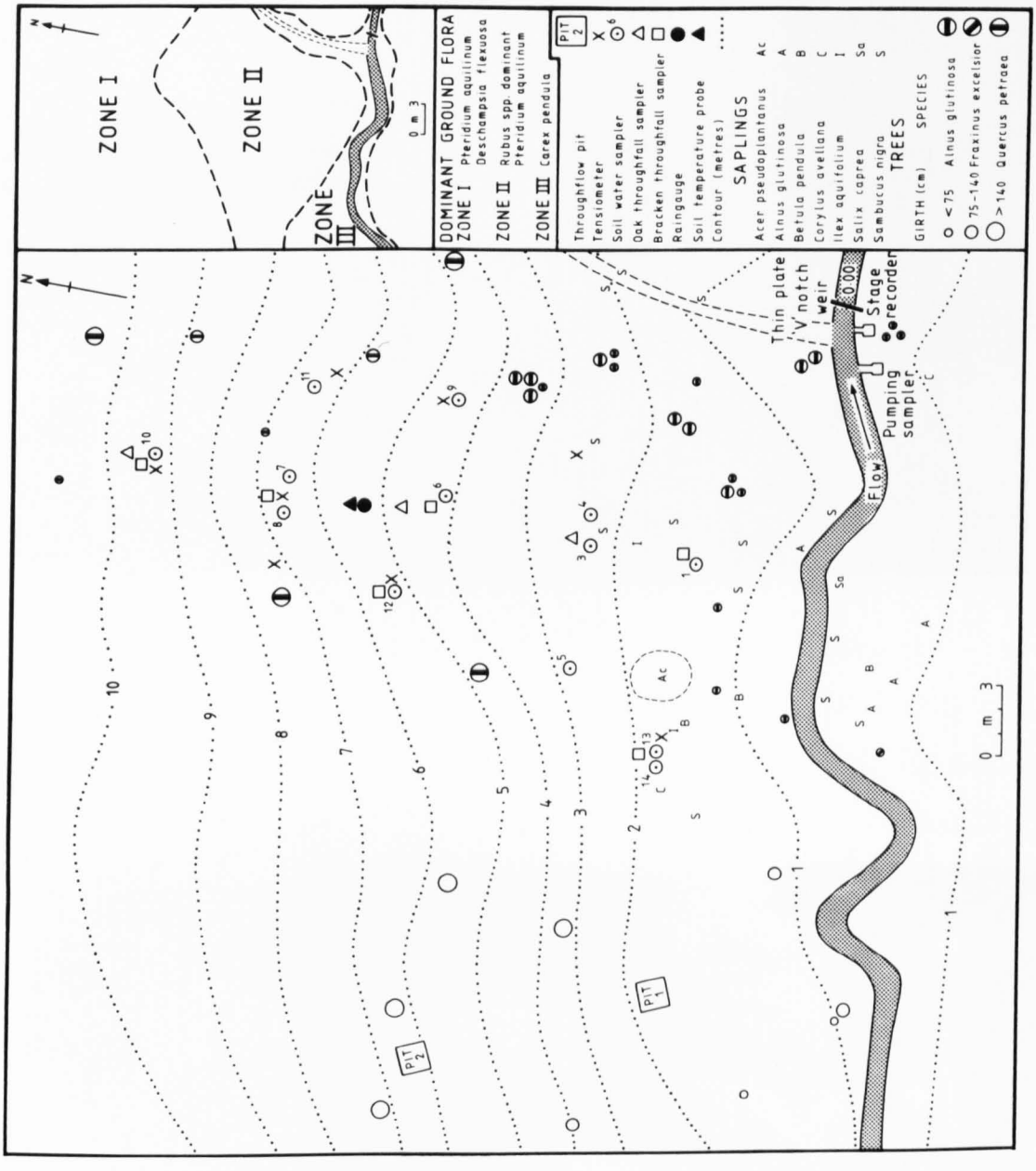


Figure 2.17 Instrumented hillslope section site 1

Figure 2.18

Figure 2.18A View across hillslope site 1

Figure 2.18B Stream and instrumentation

provided that the connecting drainpipe was kept clear of sediment and other blockages. A continuous record of the stream stage was obtained on the drum chart and this was checked at weekly intervals by measuring the height or stage of water flowing over the V notch weir. Discharge was calculated after constructing a rating equation of stream stage with discharge, measured using an OTT current meter at 0.6 depth at intervals across a measured cross section. This type of equipment is the most common in use for gauging flow and was found to be completely reliable (Figure 2.19A).

A weekly grab sample of stream water was taken at a point just downstream of the weir and more detailed information on stream chemistry was obtained using an automatic vacuum sampler set at 8-hourly intervals. The instrument was obtained from Automatic Liquid Samplers Ltd ^{R} and was operated by introducing a vacuum into a system of twenty four bottles. A timer operated a stepper drive motor which released a vacuum in a numbered sequence of bottles at the required time interval. The result was to draw in a sample of stream water which remained in the collecting bottle until the bottle was emptied. Significant gaps in the samplers records were caused by many recurring faults particularly with the timing mechanism shown in Figure 2.19B. Figure 2.18B shows the positions of the stage recorder and automatic sampler in their housing boxes next to the stream.

2.2.4 Vegetation and Soil Inputs

The fluxes and chemistry of water within the drainage basin are described in Sections 2.2.1 to 2.2.3 and these parameters may be influenced by the seasonal growth of vegetation and soil properties; the experimental framework (Figure 2.7) illustrates the relationship between vegetation and

Figure 2.19A Stage recorder

Figure 2.19B Vacuum sampler

soil inputs to the hydrological parameters and the following subsections describe the procedures used to obtain samples representative of the hillslope vegetation and soil.

i) Vegetation

Vegetation exhibits considerable variation in elemental composition due to age, plant component and season. A sampling scheme was devised whereby vegetation was obtained on 19 occasions between June 1980 and December 1981. A larger sampling scheme though desirable may have markedly affected the overall structure of the bracken community by increasing the detrimental effects of trampling. Newbould (1967) recommends 8 to 12 samples per year with the sampling period reduced during periods of rapid change. In this study the sampling interval ranged between three to seven weeks depending on season. All vegetation was collected whilst wearing plastic gloves and samples were placed in sealed polythene bags to reduce contamination.

Bracken fronds and rhizomes, litter and the associated soils from the Ah and Bt(g) horizons were sampled from four separate $1m^{-2}$ locations. A fixed coordinate grid system was drawn up for the sampling area and random number tables were used to determine these plots. Fronds were harvested by cutting the rachis at the point of entry into the litter layer. The total fresh weight for each square was determined using a spring balance and then a subsample of fronds was taken for analysis. Frond fall was defined by the time at which the fronds were brown in colour and the rachis had folded over. During the autumn and winter months of 1980-81 a litter sample of the 1980 growth was taken

for each metre square. Bracken rhizomes and roots were harvested in the same random quadrats as the fronds using a purpose designed corer (Figure 2.21). The corer consisted of a 12.7cm diameter, 30cm deep, mild steel cylinder with a sharpened cutting edge. A T-piece across the cylinder acted as foot rests and this was welded to a shaft and handlebars. The equipment was painted to prevent rusting. The corer was driven into the ground in a similar manner to a spade to 30cm depth and two separate cores were taken within each square. Live rhizomes and roots were removed and placed in polythene bags. The sampling and estimation of root biomass is tedious and can be destructive to the plant community as a whole (Newbould, 1967). Ellis and Barnes (1971, 1973) recommend the separation of roots from soil using soil corers which should have a minimum diameter of 5cm. Problems of root separation and identification did not occur as rhizomes and roots are easily recognised. Watt (1940) states that the maximum depth of rhizomes in the soil depends on local conditions of climate, soil type and other vegetation and in soils of poor nutrient status rhizomes will accumulate in the surface horizon and no rhizomes were found below 30cm in this study.

Ground litter was also sampled using the large corer as this enabled a crude estimate of biomass accumulation and decomposition. The litter was separated from the two cores and included the surface litter, fermentation and humus layers. The humus layer was easily distinguishable from the Ah horizon by its colour and texture. Samples were bulked for each square and no separation of litter components was made.

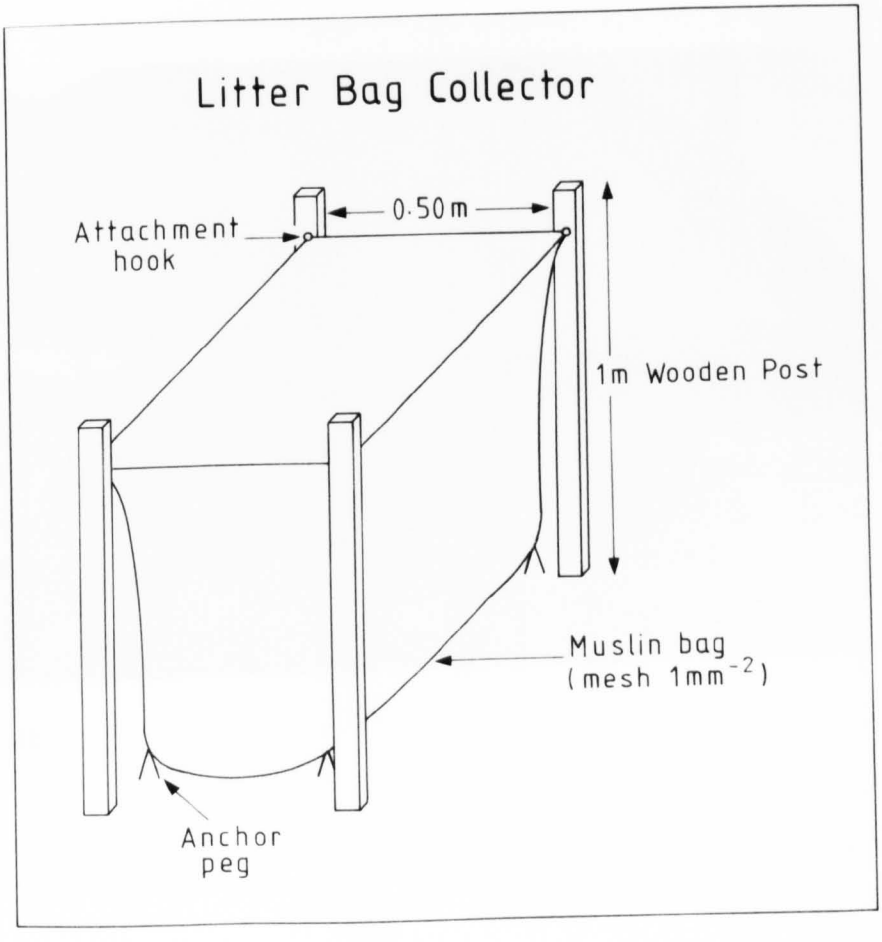

Litter Bag Collector
Attachment hook
0·50m
1m Wooden Post
Muslin bag (mesh 1mm⁻²)
Anchor peg

Figure 2.20

Christmas Corer
Rubber cycle grips
Handle bars
0.1m
0.1m
0.30m
0.127m diameter
Foot rest
Cutting edge

Figure 2.21

Methods for the calculation of tree biomass and nutrient accumulations are complicated and require destructive sampling techniques for reliable estimates (Newbould, 1967 and Whittaker et al, 1974). This procedure was not necessary as only the annual growth and associated nutrient uptake and release were of interest in this project. The annual growth of oak was sampled by taking randomly picked twigs, buds and leaves from several trees. Johnson and Risser (1974) have shown that there is no difference in the nutrient status of leaves and twigs and therefore samples were not separated into the various components. The annual leaf biomass was calculated using the litterfall method (Newbould, 1967) where the total amount of leaf litterfall is calculated from the subsamples caught. Litterfall throughout the year was also sampled.

Litterfall collectors vary in design from small funnels to large plastic sheets placed on the ground surface. Carlisle, et al (1966a) used 20, 20cm diameter, polythene funnels raised up to 36cm on wire frames and larger fractions of litter were caught in 15 $0.16m^{-2}$ wooden frames lined with punctured polythene sheets. Johnson and Risser (1974) used similar $1.0m^{-2}$ wooden boxes with a screen bottom, placed on larger polythene sheets to prevent contamination of the contents by soil splash but this type of collector is susceptible to loss or gain of litter by blowing wind. Gosz et al (1972) used 45 traps of $0.224m^{-2}$ consisting of a removeable muslin bag placed on a 0.53m diameter hoop. The bag rim was placed 1.5m above the ground surface and the bag bottom stabilised using a clothes peg to prevent loss by wind blow. The necessary requirement of a litter collector is to allow rainwater to pass quickly through the collector otherwise excessive

leaching and accelerated decomposition may occur. The collector must also be protected from the effects of splash and wind. In this experiment three muslin bag collectors (Figure 2.20) of $0.25m^{-2}$ were placed at randomly chosen locations (Figure 2.10) on the hillslope, supported by 1.0m high wooden stakes. The bag bottom was attached to the ground using a piece of string tied to an embedded stake. These collectors caught samples of litter including twigs and small branches and allowed water to drain quickly. The number of collectors used in this experiment was low compared to other studies but these were specifically designed to study litterfall. Litterfall bags were emptied at the same time as other vegetation was sampled with the exception of autumn months when abscission was at maximum and fortnightly samples were taken. No separation of litter fractions was made but a note of composition was made.

The amount of defoliation of oak trees by larvae and insects was estimated using the method of Carlisle et al (1966a). 200 oak leaves were sampled immediately after the cessation of defoliation on 24 6 81. Total fresh weight of the leaves was determined and each leaf was photocopied. The remaining leaf area and mid rib length were measured using a planimeter and chartometer respectively. The original leaf area was estimated using the equation of Carlisle et al (1966a). The dry weight was determined and the amount of defoliation calculated. The frassfall which resulted from the activity of phytophageous insects contaminated throughfall samples and therefore a subsample of the frass itself was obtained by placing a $1m^{-2}$ plastic sheet collector in a wooden framework on the litter surface. The sample was used for chemical analysis and biomass estimation.

ii) Soils

The value of laboratory data in soil studies depends on an effective sampling scheme where every sample represents a definite body or class of soil that is as homogeneous as possible (Avery and Bascomb 1982). Most soil types exhibit a high degree of spatial variability even within a small area (Ball and Williams, 1968). This is an important concept to this study as inherent variability may mask seasonal variation in nutrient levels. Consequently an extensive survey of site variability was necessary, the results of which are presented in Chapter 5. A soil sampling scheme was then devised which would not only monitor nutrient levels from a constant source throughout the study but also relate to the actual growth and nutrient cycling of bracken.

The variability study was made by taking random samples based on a grid system and at least 6 individual cores were taken from the Ah and Bt(g) and BCg horizons for 6 sites and then bulked for each site. Chemical analysis was performed on collected soils (Chapter 3.0) and then the 95% confidence limits were established which provided upper and lower levels of natural variability in the A and B horizons.

Soil samples from the Ah and Bt(g) horizons were obtained using the large corer described in the previous section from the vegetation sampling squares. The properties of these soils could therefore be directly related to the vegetation characteristics. Figure 2.10 identifies a soil sampling area where samples of the A and B horizons were taken at fortnightly intervals using a 3.5cm diameter cylindrical auger (Figure 2.14A). This type of auger

allows easy identification of soil horizons. Sampling from this constant source area aimed to identify changes which were not associated with spatial variability. It was recognised, however, that a large proportion of spatial variation may occur within a small area (Beckett and Webster, 1971) and the identification of such changes might not be possible.

Chapter 3 ANALYTICAL TECHNIQUES

3.0 Introduction

Ecological materials are susceptible to chemical and physical deterioration after collection and therefore analytical techniques, or storage, were commenced within 24 hours. Various analytical problems were encountered with each sample type and these are described in the three main sections of vegetation, soils and water. All analytical techniques provided a soluble extract which enabled comparative elemental analysis for each sample type. Routine chemical determinations for all samples included calcium, magnesium, sodium, potassium, ammonium, nitrate, nitrite, chloride and phosphate; total nitrogen in vegetation. pH and specific conductance were measured in water samples and oxidizable organic carbon in soils. Section 3.2 describes the non-routine chemical determinations which were made to characterise soil properties. The moisture content of soils and vegetation samples was also recorded routinely. An evaluation of the techniques used is presented, using reproducibility and comparability tests.

3.1.0 Vegetation

Laboratory analysis of vegetation samples entailed biomass estimation and nutrient analysis. The vegetation samples analysed were bracken fronds and rhizomes, oak leaves and twigs, litterfall and bulk litter samples which included L, F and H layers. High quality control was maintained throughout the experiment to help minimise sample contamination, for example, plastic gloves were always worn when handling vegetation and samples were stored in sealed containers.

3.1.1 Sample Preparation - Vegetation

The fresh weight of all vegetation samples was first recorded. No samples were washed prior to analysis to remove surface contamination, as nutrient loss by leaching or washing of exudates can seriously reduce nutrient concentrations (Likens and Bormann, 1970 ; Allen, 1974). Soil particles on roots were brushed off after drying. Samples were oven dried at 80^{o}C in cheese cloth bags or foil trays for 24 hours; higher temperatures can cause the denaturing of compounds and give rise to the release of elements (Allen, 1974). The moisture content as a percentage of dry weight was calculated and samples were subsequently ground using a ball mill and macerator. All samples were passed through a 0.5mm sieve and stored in clean, screw top glass bottles at a temperature of 6^{o}C. Subsamples for analysis were ground to a fine powder using a pestle and mortar, placed in an oven at 80^{o}C for three hours and cooled in a desiccator. This procedure enabled chemical analysis without the necessity of adjusting results for air dry moisture content.

3.1.2 Acid Digestion

A sulphuric acid-hydrogen peroxide digestion was used to prepare samples for nutrient analysis. This technique has several advantages (Allen, 1974); first there are no volatilization losses of metallic elements such as sodium and phosphorus, secondly, the procedure is fairly rapid and is easily adapted for routine work, and lastly a large number of nutrients, including nitrogen, can be determined from one digest solution. Sulphuric acid is used to prevent complete evaporation of the hydrogen peroxide solution and thus minimises the danger of explosion. The method was developed by the Chemical Section of the Institute of Terrestrial Ecology and is suitable for samples containing significant amounts of liquid, such as bracken. Selenium, the catalyst and lithium sulphate are used to raise the digestion

temperature and ensure the complete conversion of nitrogen to ammonium sulphate. Allen (1974) states that precipitation of potassium as perchlorate and calcium as sulphate should not occur providing the correct weights of sample are used. Litter samples and to a lesser extent, rhizome samples, contained varying amounts of silica and incomplete recovery of nutrients may have occurred due to the formation of silicates of potassium and aluminium. The silica content of samples was determined from filter papers after the digestion procedure was completed and sample weights adjusted accordingly The alternative procedure of digestion with hydrofluoric acid was not desirable on a routine scale.

Approximately 0.4g of powdered sample was digested with 4.4ml of acid-peroxide mixture in a 50ml kjeldahl flask for three to four hours. After cooling all samples and a blank solution were diluted to 250ml and filtered. All digests were then analysed according to section 3.4.0 with nitrogen analysed as ammonium. The Chemistry Section at the Institute of Terrestrial Ecology, Merlwood, has performed chemical analyses on bracken and oak for several research projects, Frankland (1976), Callaghan et al (1981) and Chen and Lindsey (1981), and their laboratories were visited to observe the procedures used to ascertain standard methodology. Recovery rates of nutrients for this technique were investigated by comparison with the dry ashing method described by Likens and Bormann (1970). Significant correlations at the 99% level were obtained for calcium, magnesium, sodium and potassium.

3.2.0 Soils

Moisture content, carbon and the nutrient content of soils in soluble and exchangeable form were determined on a routine basis for all soil samples. Further non-routine analyses which characterised soil properties are also described.

3.2.1 Sample Preparation - Soils

In the laboratory soils were placed in soil trays, weighed and allowed to air dry to determine the moisture content as a percentage of dry weight. Soils were then ground using a mortar and pestle and passed through a 2mm sieve. The analytical problems associated with air drying of soils should be recognised: in particular extractable phosphorus and potassium may increase after drying whilst nitrogen and phosphorus should ideally be determined from fresh soil (Hesse, 1971). However, the nutrient concentrations of a soil can change over a relatively short period of time in response to variations in rainfall, drainage and temperature. In order to compare soils it is essential to standardise by air drying (Hesse, 1971). The length of drying time is also critical to nutrient levels in soils; organic nitrogen, for example, is mineralised on rewetting and the amount released increases with length of drying time. Therefore soils were dried and analysed within a fortnight of sampling.

3.2.2 Chemical Determinations

i) Water Soluble Ions

Water soluble ions are normally extracted to give a measure of salinity which can be harmful to plant growth. In this study the purpose was to identify those ions which may be present in the soil water solution as opposed to those which were held on exchange sites. These ions are readily available to plants but are also susceptible to leaching and removal from the upper soil horizons by percolation or lateral flow. The extracted ion, however, may also include an indeterminate proportion which is loosely bound to exchange sites. A 1:5 ratio of soil to deionised water was mechanically shaken for exactly 30 minutes and then immediately filtered through a Whatman GF/C glass fibre filter

paper. The timing was critical otherwise a greater proportion of exchangeable ions may be included in the extract. This is not an entirely satisfactory method of obtaining a soil solution as in their natural state solute concentrations are dependent on soil water residence times (Trudgill et al, 1981), a problem which is discussed more fully in Chapter 5. Soil water samples were also obtained using suction lysimeters and a correlation of nutrient concentrations from these samplers and soil water extracts is presented in Chapter 5.

ii) Exchangeable Cations

A Ammonium Acetate Extraction

The conventional method of extracting cations with 1M ammonium acetate (pH 7.0) was used to determine exchangeable calcium, magnesium, sodium and potassium. Soils were placed in leaching columns and the solution passed through at a constant rate as recommended by Schollenberger and Simon (1945) and Tinsley (1970). Whilst this is a well established method of extraction the recovery rate is not complete; specific problems relate to particle sizes, the solubility of associated anions and internal reactions with colloidal constituents may occur (Schollenberger and Simon, 1945). The leachate will contain cations exchanged from the soil plus an unknown amount entering by simple solution; however, the technique does provide a means of identifying the dynamics of nutrients on soil exchange sites.

B Sodium Chloride Extraction

Exchangeable ammonium was extracted using a 1M sodium chloride solution on air dried soil (Allen, 1974). The determination should be made with fresh soils as drying leads to the loss of free ammonia and microbial activity may utilise a certain amount. The acidity of the soil sample increased the probability of absorption of ammonium from the atmosphere and filter papers. Therefore samples were not filtered but allowed to settle and an aliquot pipetted off for analysis.

iii) Soluble Phosphorus

Phosphate levels in British soils are traditionally low, but as it is one of the major plant nutrients its study has been extensive. Up to 96% of soil phosphate is unavailable to plants and no satisfactory method has yet been developed for the extraction of available phosphate. Many different extractants have been used in the past and are evaluated by Hesse (1971). Iron, aluminium and manganese hydroxy-phosphates are probably the main form of phosphorus in this soil because soil pH is well below 5.5. Phosphorus in this form is largely unavailable and extraction of the soil with an acid solution provides an extract with a phosphorus concentration similar to that of the soil solution. Therefore a 0.01N solution of glacial acetic acid was employed (Tinsley, 1970) in preference to the sodium bicarbonate extractant recommended by the Soil Science section of MAFF, Wolverhampton (personal communication). This latter method required a critical constant temperature which could not be achieved with the facilities available. It is recognised that the amount of

phosphorus can increase with drying. Since the levels of phosphorus in these soils were low and occasionally undetectable, the loss of phosphorus by drying was not considered an important factor.

iv) Organic Carbon

Oxidisable organic carbon includes the immediate decomposition products of organic material and soil humus and excludes inorganic and elemental forms; it is the oxidisable form which is chemically active in the soil and litter zones. The Walkley and Black method, as described by Hesse (1971) was used to determine organic carbon and is a modification of the original experiment by Schollenberger. In the former method a mixture of dilute potassium dichromate and concentrated sulphuric acid provide the heat reaction to oxidise a percentage of the total organic carbon. Whilst only 76% of the total organic carbon is recovered, it is more selective than any other method as only 10% of elemental carbon is included in the analysis (Bremner and Jenkinson, 1960). A correction factor of 1.33 is recommended (Bremner and Jenkinson 1960; Hesse, 1971) for conversion to total organic carbon. Percentage recovery was not known for this experiment and results quoted are therefore representative of oxidisable organic carbon and not total organic carbon. There are several elements which interfere with carbon determinations and these include chloride, nitrate, iron and manganese. Chloride competes with organic matter in reducing the chromic acid; 1 m.e. of chloride being equal to the reducing potential of 3.5 m g of carbon. No correction was made for chloride interference in the soil analyses since at measured chloride levels only a maximum of

1% error in carbon content would have resulted (Hesse, 1971). Nitrate did not interfere as its ratio to carbon was less than 1:20 and manganese levels were too low to interfere. The addition of phosphoric acid before titration suppressed the influence of iron. Because the recovery of carbon is dependent on the heat of reaction all samples were allowed to cool for exactly thirty minutes after the addition of the oxidising agents. The above analyses were performed routinely on all soil samples. A series of further experiments were performed on the Ah, Bt(g) and BCg horizons of bulked samples from the site variability experiment, to identify other important soil properties.

v) Total Nitrogen

Soil samples were digested in Kjeldahl flasks after pretreatment with water, using an acid digestion method recommended by Avery and Bascomb (1982). This method converts all nitrogen compounds to ammonium, including those which might normally be insoluble due to cementing material. The digest was distilled using Hoskins apparatus (Tinsley, 1970). The distillate was titrated with standardised 0.01N hydrochloric acid and the percentage nitrogen calculated. Bremner and Shaw (1955) investigated the accuracy and efficiency of the Kjeldahl procedure and concluded the standard method gave consistent results.

vi) Total Phosphorus

Metson (1956) states that the total phosphorus in soils rarely exceeds 0.2%, with the organic form usually predominating. A simple perchloric-nitric acid digestion method was chosen to determine total phosphate and concentration was determined using the molybdenum blue method (Hesse, 1971).

vii) Cation Exchange Capacity

The rapid method recommended by Hesse (1971) was employed using sodium as an index ion. The method involves repeated dispersal and centrifuging of soil samples with sodium acetate. The residual sodium acetate is removed with ethanol and then sodium ions are extracted with ammonium acetate. The results are comparable with the more conventional methods of E.D.T.A. titration (Avery and Bascomb, 1982) and leaching (Tinsley, 1970) provided care is taken to ensure adequate dispersion and shaking of the sample as some soils may become cohesive (Hesse, 1971). Sodium concentrations were determined and cation exchange capacities calculated as m.e. $100g^{-1}$.

viii) Soil Reaction (pH)

Soil pH was measured using 1:2.5 w/v suspensions (Avery and Bascomb, 1982). Two measurements were made for each sample, one in deionised water and the second in 0.01M calcium chloride. The latter measurement aims to standardise the effect of salt concentration by adding an excess of salt, which destroys the electric double layer of soil particles. The routine measurement of pH to monitor seasonal changes due to plant activity is fraught with many difficulties, which include the varying effects of carbon dioxide production by microbes and root systems, hysteresis, plant nutrient uptake and release, and gleying. In addition there are the inherent problems of the laboratory analysis itself (Hesse, 1971). pH determination on fresh soil samples was not possible and therefore was only measured as an indicator of acidity.

3.2.3 Physical Determinations

i) Particle Size Analysis

The wet sieving and pipette method on the less than 2mm soil fraction was chosen to determine particle size distribution on samples from the Ah, Bt(g) and BCg horizons as well as two drift (Cu horizon) samples obtained from Borehole 1 at 140cm and 310cm (Avery and Bascomb, 1982). Samples were peroxide treated to remove organic matter and the dithionite-citrate system of extraction was used to remove iron oxides (Avery and Bullock, 1977). Table 3.1 summarises the particle sizes identified.

Table 3.1. **The range of particle sizes identified**

Particle size	Particle type	Method of Analysis
600um - 2mm	coarse sand	wet sieving
212 - 600um	medium sand	wet sieving
63 - 200um	fine sand	wet sieving
2 - 63um	silt	pipette method
2um	clay	pipette method

Results for each size fraction were expressed as a percentage of the total soil and soil texture was identified using the textural classification of the Soil Survey (Hodgson, 1974).

ii) Clay Mineralogy

The X-ray diffraction method is the most widely used for the identification of clay minerals. When organic matter, carbonates and iron oxides are removed soil clay consists mainly of

crystalline layer lattice structures, each having its own characteristic atomic structure which diffracts X-rays in a unique pattern. A 20ml sample of each of the 2um clay fractions from the particle size analysis were placed in crucibles and freeze dried for forty eight hours. This method of drying is necessary as oven drying can destroy the crystal lattice structure of the clay minerals. The method of Avery and Bullock (1977) was followed which recommends five different slide preparations for each soil, so that clay types with similar properties which may conceal each other in the analysis can be separately identified. This is a complicated technique which is easily invalidated by inexpert interpretation and, as the Department had no experience of mineralogical studies, the Soils and Plant Nutrition section at Rothamsted Experimental Station was visited for advice and instruction prior to the determination. Slides of orientated aggregates of clay from the Ah, Bt(g) and BCg soil horizons were prepared so that crystal basal planes were orientated approximately parallel thus emphasising the diffraction. Comparison of slides was made possible by ensuring an equal amount of clay suspension was placed on X-ray slides of the same surface area. The rationale for each slide treatment is explained by Grim (1962), Brown (1972) and Avery and Bullock (1977). 335^{o}C and 550^{o}C treated samples were placed in a cold muffle furnace, heated to the relevant temperature and allowed to cool in the furnace without opening the door so that blistering of the clay suspension did not occur.

Initially X-ray photographs using CuK radiation were made on air dried slides to identify the clay minerals and ensure the validity of the preparations. The standard diffraction spacings in Angstrom units (Å) for each mineral were identified using Braggs Law.

Equation 3.1:

$$n\lambda = 2d(hkl) \sin \theta$$

where d (hkl) is the true lattice spacing for the plant

λ is the wavelength

n the order of the reflection

tables were available for this conversion (Parrish and Mack, 1963). Values are converted to Å because θ, the angle of incidence, can vary according to the wavelength used and the results would not otherwise be comparable. This method does not provide a means for semi-quantative analysis, therefore a linear diffraction trace was made for every slide preparation using a Phillips diffractometer. This apparatus was operated using a proportional counter, pulse height selection, CuK radiation scanning from 2^{o} 2θ at a time constant of one second. Avery and Bullock (1977) recommend the use of a $1/4^{o}$ divergence slit throughout the scan but this was not possible due to the insensitivity of the scan. Therefore a $1/6^{o}$ slit was used for the first 10^{o} scan and then the $1/4^{o}$ slit was installed for the remaining scan up to 70^{o}. The equipment was checked for accuracy using a monochromating crystal, a quartz standard, confirming the known value for the diffraction spacing. Operating conditions varied according to the sample and its original treatment. The crystal lattice structure

of some of the expanding clay minerals is known to be influenced by humidity (Brown 1972), therefore a small amount of phosphorus pentoxide, an effective drying agent, was placed in the X-ray chamber for each X-ray scan. Avery and Bullock (1977) recommend the heating of the 335^{o}C + 550^{o}C treated slides to 120^{o}C during diffraction. However, these facilities were not available but the inclusion of phosphorus pentoxide adequately prevented the entry of moisture into the lattice layer.

Standard diffraction spacings were obtained from peak positions and the estimated strength of reflection noted. This information enabled the clay minerals to be identified from a powder diffraction file (Berry, 1974). The quantative determination of clay minerals cannot be made as individual minerals vary in mass absorption, orientation of grains, crystal perfection and chemical constitution, all of which affect radiation intensities (Grim, 1962). A semi-quantative estimate was made by weighting peak areas - a method described by the Soil Survey (Avery and Bascomb, 1982). The estimation is aided by interpretation of cation exchange capacities and non-exchangeable potassium which in mineral soil are dependent on clay type.

3.3.0 Water Samples

Water samples are unique in that they do not require the same initial treatment and preparation as vegetation and soils, but certain problems arise after collection. Chemical changes which occur during collection and problems of preservation are important considerations. Allen (1974) states that most water occurs as a relatively homogeneous medium because of thorough mixing in its turbulent state and therefore analysis problems encountered with soil and vegetation do not arise.

3.3.1 Sample Preparation

Previous workers have shown that the chemical composition of waters stored in the laboratory can alter quite significantly, due to evaporation, microbial activity and complexing reactions. Allen (1974) states that pH, conductance, nitrate and phosphate are very susceptible to change and should be analysed within 24 hours. Galloway and Likens (1976) found that little change occurred in rainwater at a variety of storage temperatures with the exception of phosphate and chloride. These storage problems are also applicable to water samples which are 'stored' in the field until the weekly collection occurs. All water analyses were performed within 48 hours of collection with pH, phosphate and nitrate being given priority . Fine suspended material found in natural water samples is usually organic in nature and consists of colloidal material which has been floculated by bacteria and protozoa. The inorganic material is usually silicious and originates from weathered soil (Allen, 1974). The removal of this material is necessary as it may affect concentrations of ions and can also cause blockages in analytical equipment. All water samples, soil and vegetation extracts were filtered through a Whatman glass fibre GF/C filter paper using a Hartley-type Buchner funnel and vacuum apparatus.

3.3.2 Chemical Determinations

i) Water Reaction (pH)

pH was determined on water samples using a Corning Model 12 glass electrode meter prior to filtering. The meter was buffered at pH 4.0 and 7.0 before each set of measurements.

ii) Specific Conductance

Specific conductance measured as microsiemen cm^{-1} ($\mu S\ cm^{-1}$) was initially measured using a WPA CM25 meter which required temperature correction to $25^{o}C$. In the latter part of the project a PT1-18 Digital Conductivity meter was used which automatically compensated for temperature. Comparison of two weeks' results for a variety of samples for both meters showed no significant differences at the 99% confidence level. All water samples including soil water extracts were tested for specific conductance providing an indication of the total amount of ions in a solution. On the basis of work by Foster, Grieve and Christmas (1981) using samples from this drainage basin, it was decided not to estimate total dissolved solids from specific conductance. A copy of the published paper is appended to this thesis.

iii) Dissolved Organic Matter

The amount of dissolved organic matter in water samples is related to the interaction of plant growth and decomposition and water fluxes within the ecosystem. Measurement of this property indicates the level and location of interaction. The Walkley-Black method for determining dissolved organic matter in water samples (Hesse, 1971) is an involved process and for routine determination on all water samples would have been too time-consuming. An alternative method proposed by Smart et al (1976) offered a rapid method of analysis using an ultra violet fluorimeter to detect the natural fluorescence of organic molecules. A range of water samples was analysed by both methods for eight consecutive weeks and the results of each

method incorporated into a simple linear regression model. Whilst a highly significant correlation at the 99% level was found for samples with low dissolved organic matter, no significant correlation could be found for solutions with high concentrations. The latter samples, for example, throughflow which have strong colouration, are unstable and may fade, darken, or precipitate compounds. The presence of iron or low pH values may also interfere with results. This technique was therefore unreliable for the range of water samples found at Atherstone and because insufficient time was available dissolved organic matter was not determined on water samples, though data was available from Site 1.

3.4.0 Analytical Methods

Vegetation and soil extracts and their blanks were analysed in the same manner as water samples for solutes. The techniques are presented followed by a discussion on the reliability of the equipment used.

3.4.1 Solute Analysis

i) Calcium and Magnesium

Calcium and magnesium concentrations were measured on an EEL140 atomic absorption spectrophotometer, using air and acetylene fuel. Several elements interfere with the absorption of calcium and magnesium particularly phosphorus, aluminium and iron whilst acidity also affects values. Calcium and magnesium can be isolated by precipitation or percolation through ion exchange columns but neither method is convenient for routine analysis (Allen 1974). Strontium and lanthanum have been used as

releasing agents which counteract depression effect (Likens et al, 1969). Treatment of selected samples with lanthanum showed no significant increase in calcium or magnesium concentrations at the 99.9% confidence level, illustrating that interfering elements were not present in sufficient quantities.

ii) Sodium and Potassium

Sodium and potassium were measured using an EEL Flame Photometer Mark II. Interferences are minimal to these elements and extractant influences are compensated by the measurement of a blank sample. Very high calcium levels give positive errors but this was not a problem in this study. The EEL Mark II is a sensitive instrument and can detect levels as low as 0.01 mg l^{-1}.

iii) Ammonium

Ammonium was initially measured in the project using a method recommended by Truesdale (1971), where ammonium is reduced to nitrite and forms a pink azo compound. However, it was found that the carbon colouration in many samples distorted colourimeter readings and the production of blank samples was very time-consuming. As an alternative, ammonium was measured using an Orion model 95-10 selective ion probe. This is a gas sensing probe which measures ammonium levels after conversion to ammonia. Colour and turbidity do not affect measurement and Kjeldhal digestions can be analysed directly without distillation. Interfering ions such as cobalt, copper and mercury were precipitated using 10M sodium hydroxide. The method is temperature dependent with a $1^{o}C$ difference giving a 2% error and samples were therefore analysed when at room temperature.

Care was taken to minimise losses of ammonia to the atmosphere by immediate analysis. Results were obtained by plotting a semi-logarithmic calibration curve and were expressed as ammonium, the form which exists in the field.

iv) Nitrate, Nitrite and Chloride

Nitrate and nitrite were analysed on a Chemlab auto-analyser by a method based on the formation of a pink azo dye which is determined colourimetrically. The determination of nitrate and nitrite both present in a solution was carried out by determining nitrite alone and then by reducing all nitrate to nitrite using a hydrazine copper reagent. Nitrate was determined by abstracting nitrite from the total oxidised nitrogen. The equipment can operate over two ranges 0-1 mg l^{-1} and 0-100 mg l^{-1} of nitrogen, the latter with the use of a dialyser.

Chloride was also measured on a Chemlab auto-analyser, the method was based on the ability of chlorides to release thiocyanate ions when reacting with mercuric thiocyanate. The colouration produced by ferric sulphate was determined colourimetrically and a range of 0-40 mg l^{-1} can be detected with a high level of accuracy. The samples which contained large quantities of dissolved organic carbon had a similar colouration to the reaction compound and therefore blank determinations were also made. Nitrate is known to interfere with this reaction causing a 5% error for any equivalent amount of chloride present, but no correction factor was used in this project.

v) Phosphorus

Colourimetric methods determine phosphorus as orthophosphate and two main methods are available. The vanomolybdate method was initially used but it was too insensitive and the yellow colour developed was often indistinguishable from the natural colouration of some samples. Phosphorus was therefore measured by the molybdenum blue method (Allen, 1974), which develops a heteropoly-phosphomolybdate compound when acid molybdate is added to a solution containing orthophosphate. The time for the development of the blue colour is critical (20 minutes) and the procedure recommended by Tinsley (1970) was adopted. The developed colour was measured at 640 nm on a Corning EEL Model 197 colourimeter. There are many problems involved in the determination of phosphorus, for example labile phosphorus can become fixed as insoluble phosphate and therefore is not detected in available phosphate determinations. Silicates and arsenates give similar colours to phosphorus in the reaction, silicates were suppressed by the acid reaction and arsenates were probably not applicable to this study. Iron in quantities greater than 10 mg l^{-1} will depress colour but this again was not relevant and the maximum value detected in any sample was only 2.0 mg l^{-1}. Phosphorus levels were extremely low in many samples and great care was taken to prevent contamination in the laboratory. It was found that certain plastic cuvettes for the colourimeter released phosphates into the sample and consequently the use of a better quality container prevented this contamination.

3.4.2 Fluorescent Dye Detection

The fluorescent dye tracing experiment commenced on 30th September 1981 and filtered soil extracts and water samples which potentially contained the fluorescent dyes Lissamine FF and Sulpho-rhodamine B were examined for fluorescence routinely until the end of the project. A Perkins-Elmer 3000 Ultra Violet fluorimeter was used and no sample pretreatment was necessary as only qualitative data was required (Smart and Laidlaw, 1977). Lissamine FF was identified at 420nm excitation, 515nm emission spectra and sulpho-rhodamine B at 565nm excitation, 590nm emission spectra. The natural fluorescence of dissolved carbon in samples did not interfere as the emission spectra fell between 400 and 460nm. The dye spectra were identified using standard solutions of the dyes in deionised water. Samples containing any quantity of either dye were excluded from the solute analysis.

3.4.3 Units of Measurement

A calibration curve was constructed for each analytical technique using a range of standard solutions and blank determinations for background correction were made where necessary. The co-ordinates for each standard were read into a PET micro computer and then unknown readings were computed as milligrams per gram of vegetation, milliequivalents per 100 grams for soils (me $100g^{-1}$) and milligrams per litre for water samples (mg l^{-1}). Further data manipulation was performed using a main frame computer which calculated biomass and nutrients as kilogrammes per hectare (kg ha^{-1}).

3.5.0 Validation of Results

In order to establish the accuracy of the analytical techniques used, a

series of experiments was devised whereby analysis was performed on replicate samples of soil, water and vegetation. The deterioration of water samples in the field was investigated and compared with ion exchange method of solute preservation.

i) Reliability of Techniques

Six fold replicates of a rainfall sample, bracken frond and soil extracts from the Ah and Bt(g) horizons were analysed for all nutrients and Table 3.2 shows the percentage coefficient of variation calculated for each sample nutrient.

The rainfall sample exhibits the least variance for each nutrient with the exception of phosphate. Water samples are homogeneous in solute composition and therefore the variance identified probably represents the reproducibility of the analytical techniques. Results for the phosphate analysis for all samples are high and this illustrates the problems involved when detecting low levels of phosphate especially in the water and soil water samples. The frond sample exhibits slightly more variance than the water sample, but generally illustrates the small variability between sub samples. Soil samples show the greatest variance and this is attributable to the heterogeneous properties of soil particles and their ability to release exchangeable and water soluble ions.

The variance of the reproduciblity experiments is fairly high, but this is probably not a reflection of the experimental technique but of the inherently low concentrations of solutes in the analysed sample.

Table 3.2. **Percentage coefficients of variation for replicate analysis**

		Ca	Mg	Na	K	NH_4	NO_3	NO_2	Cl	P	pH	SC	Carbon
Rainfall		10.8	14.0	4.6	19.8	12.5	8.7	0.0	4.2	82.2	0.61	2.2	
Bracken frond		21.5	11.4	4.9	8.1	———	31.3	———	11.9	31.5	-	-	
Soil horizon	A exch	37.9	31.9	30.7	1.0	23.7							
	A sol	43.0	9.2	3.2	3.2	51.8	38.1	-	22.9	41.5	-	2.6	2.9
	B exch	50.7	42.1	42.9	0.0	21.9							
	B sol	22.1	15.7	12.8	11.5	31.6	32.5	-	41.4	67.8	-	3.1	5.0

Table 3.3 summarises the techniques used in this study and presents figures for the manufacturers quoted accuracies. All analytical techniques become more accurate in percentage terms as the element under analysis increases in concentration. Most elements obey Beers Law, that is a linear relationship exists between concentration and galvanometer reading. At higher elemental concentrations the relationship is non linear. Occasionally the concentration of samples in solution exceeded the analytical limits quoted and therefore these samples were diluted to an appropriate level. To reduce contamination in the laboratory all glassware used was thoroughly rinsed in deionised water and sterilised disposable pipettes used for dilution. Detergents used in the laboratory were phosphate free, that is Brij35 (polyoxyethylene laurylether) and Manoxol O.T.

Table 3.3 **Summary and accuracy of analytical techniques used**

Measurement	Method	Range	Stated Accuracy
SC	Digital conductivity	0-999 µS	-
pH	Glass electrode	0-14	-
Ca + Mg	Atomic Absorption Spectrophotometry	0-100 mg l^{-1}	± 2%
Na K	Flame photometer	0-200	± 2%
NH_4	Selective ion probe	0-1000	± 2%
NO_3 - N) NO_2 - N)	Autoanalysis	0-100	± 1%
Cl	Autoanalysis	0-50	± 1%
P	Colourimetry	0-0.1	± 1%
Carbon	Digestion + Titation	0-15%	± 5%
Carbon	U.V. fluorimetry	0-15 mg l^{-1} 15-200	± 1% ± 50%

ii) Sample Deterioration

A series of experiments were designed to investigate the rate of a rainfall sample deterioration and variation within a normal sampling week and the efficiency of an alternative means of preserving ion concentration using ion exchange resin collectors (Crabtree and Trudgill, 1981).

Ion exchange resins extract ions from a water sample and the resulting deionised water can be siphoned into a storage vessel. Subsequent extraction of the resin and a knowledge of rainfall volume allows calculation of inputs. The collected sample is not subject to evaporation or microbial losses and therefore low solute concentrations in rainfall can be continuously collected over a period of time without experiencing sample deterioration. Dowex 50W-X8, 20-50 mesh (H) resin ANALR was first tested for purity by placing 10g samples in 100ml 25% v/v hydrochloric acid and also in 100ml of deionised water. The mixtures were placed in polythene bottles and automatically shaken for three hours. Blank solutions with no added resin were also tested. Determinations were made for calcium, magnesium, sodium, potassium and ammonium and results are given in Table 3.4. Both blank adjusted extracts show significant amounts of cations except potassium. Only 10g of resin in 100ml was tested and therefore a much larger error can arise in the main experiment when greater quantities of resin are used. This is a considerable source of error not initially considered by Crabtree and Trudgill (1981).

Table 3.4 **Cation exchange resin experiment**

Blank Extracts 10g in 100ml	Ca	Mg	Na	K	NH_4	SC
HCl	0.4	1.2	1.6	0	0.2	
Water	0.4	0.8	1.2	0	0.1	
Eluted Rainfall Sample						
1	0.8	0.1	0.1	0	0	74.0
2	0.9	0.3	0.3	0	0	29.0
3	0.2	0.0	0.0	0	0	82.0
Resin Extraction						
1	1.0	4.5	3.7	0.6	1.0	
2	3.7	3.2	2.8	1.1	0.8	
3	8.0	4.5	3.7	1.6	1.0	
%CV	83.4	18.5	15.3	45.5	12.4	
resin gauge $\bar{x}$	4.2	4.1	3.4	1.1	0.9	
funnel and bottle gauge $\bar{x}$	5.1	0.65	7.7	0.95	1.4	

Six polythene funnels, plugged with glass wool, and bottle gauges were spaced at regular intervals out of doors and three ion exchange resin collectors were placed in between the six ordinary gauges. The ion exchange collectors used were a modification of those by Crabtree and Trudgill (1981), so that they would be comparable with the collectors used in this experiment and the main research project; the main difference being that no vapour trap was used to minimise evaporation losses. A 500ml pyrex Buchner flask was originally used to house the resin but this was changed to a polythene bottle containing 250g of resin as the glassware was susceptible to breakage especially in the cold weather (Fig. 2.9A).

The collectors were left outdoors until a single rainfall event occurred which provided sufficient water for the experiment. On 24th October 1981 16.4mm of rain fell during the day and the next day the volumes of rainfall for each ordinary collector were measured and one third of the sample removed for analysis. The remaining samples were left outdoors but covered so that no more rainfall could enter the bottle but enabled evaporation to occur as would happen with the field site gauges. Resin collectors were also covered in the same manner and left outside for one week. After three days, half of the ordinary sample was removed and on the seventh day the final aliquot removed for analysis. Results are shown in Table 3.5. Analysis of variance was performed on the three subsamples and F values and significance levels are also presented.

Table 3.5 **Rainfall deterioration experiment**

	sample replicate	field volume	pH	SC	Ca	Mg	Na	K	NH_4	NO_3	NO_2	Cl	P
$\bar{x}$	1	16.1	6.0	104.0	5.1	0.6	7.7	1.0	1.4	1.0	0.15	12.9	0.25
%CV	1	2.5	3.9	6.2	10.0	8.4	14.0	11.0	20.2	23.6	12.8	6.9	63.6
$\bar{x}$	2	-	5.8	103.0	4.8	0.7	8.2	1.0	1.1	0.9	0.13	12.9	0.06
%CV	2	-	1.4	6.4	8.7	5.9	9.7	10.5	7.2	12.8	13.0	7.8	166.1
$\bar{x}$	3	-	6.0	109.0	5.0	0.7	7.8	1.0	1.2	0.8	0.16	10.4	0.11
%CV	3	-	1.8	11.1	6.0	7.7	15.4	8.8	28.8	39.4	72.6	6.6	109.5
F value			2.5	1.3	1.2	1.5	2.5	3.4	2.1	2.3	1.2	15.5	5.6

This table shows mean values and % coefficient of variation for each of the six samples within each replicate and F values for a one-way analysis of variance between replicates.

Critical value of F at the 0.05 probability level = 3.7

After one week the resin collectors were extracted using the procedure recommended by Crabtree and Trudgill (1981) and the resulting solution analysed. The water in the overflow bottle, the eluted sample, was also tested. Results are shown in Table 3.4

Table 3.4 shows the mean concentrations of cations collected in both the resin and the bottle and funnel gauges. The results are significantly different especially in the case of magnesium which is probably derived from the resin itself. The eluted samples also show high concentrations of ions which have not been adsorbed by the resin. The resin technique is criticised as the large amount of laboratory work and dilution involved during extraction are all susceptible to laboratory contamination and error. The rate of dilution is considerable and the extremely low values obtained are possibly beyond the detection limits of analysis. The results of this experiment show considerable variation and the technique cannot be recommended without further investigation.

Table 3.5 shows that the percentage coefficient of variation within a subsample of rainfall for each nutrient is low and does not increase over the sampling week. All variances are low with the exception of phosphorus and this has already been discussed. One way analysis of variance between the three subsamples shows that the values of F at the 0.05 probability level for all ions except phosphorus and chloride are less than the critical value and the null hypothesis cannot be rejected, that is, all the subsamples originate from the same original sample and no significant

deterioration in solute concentration can be detected. Chloride does appear to fluctuate in concentration over time and Galloway and Likens (1976) also found that chloride was the only ion which showed unaccountable variation in a similar storage experiment which was attributed to laboratory error. Variation and deterioration within this rainfall sample is minimised due to the acidity of the precipitation as hydrogen ions have a stabilising effect. In more alkaline samples deterioration may occur in the field but insufficient time was available to investigate this phenomenon

3.6.0 Conclusion

The analysis of ecological materials poses various problems which have been outlined in the previous sections. These include problems of sample storage and preservation and several techniques are criticised for their rates of recovery, efficiency and the effects of interfering ions identified. Established techniques of analysis have been adopted in this study and it is hoped that, whilst the inadequacies of the methods are recognised, the results will provide a relative data base for subsequent interpretation.

Chapter 4 HYDROLOGY

4.0.0. Introduction

Water plays a vital role as a transporting agent, solvent and catalyst in an ecosystem and therefore quantitative data on moisture fluxes is of paramount importance for an understanding of solute pathways (Likens et al, 1977). Many authors have characterised the hydrological cycle on the drainage basin and hillslope scale, for example, Gregory and Walling (1973), Carson and Kirkby (1972), Anderson and Burt (1978a) and Kirkby (1978), but the classic work of Horton (1933) was responsible for the initial formulation of ideas on hydrological pathways. Horton's model explained the movement of water in terms of the infiltration capacity of the soil. When rainfall intensity exceeded the infiltration capacity of the soil, surplus precipitation moved downslope as overland flow and was responsible for the hydrograph peak. Horton's work was based on the view that the soil surface provided an important threshold between hydrologic and geomorphic processes.

In the 1960s a variety of catchment projects were initiated in order to measure hydrological pathways in field situations, for example, Crawford and Linsley (1966), Hewlett and Hibbert (1967), McDonald (1967) and Whipkey (1965). These studies presented evidence which questioned the validity of Horton's general model in humid environments since it was established that the infiltration capacity of the soil was rarely exceeded and all workers subsequently emphasised the importance of subsurface flow and its contribution to total run-off. However, Chorley (1978) states that 'a model which takes account of post-Horton work is still awaited'. The most recent investigations have examined the diverse properties of the soil which create such a complex range of conditions for the transfer of soil

water, for example, Nortcliffe and Thornes (1978), Germann and Beven (1981), Smettem and Trudgill (1983) and Trudgill et al (1983). This recent work investigates the preferential flow pathways which water may take, for example, via macropores and other large channels such as pipes, fissures and interplanar voids. Soil water held in the finer pores of the soil matrix is only displaced when the soil nears field capacity. This type of work takes into account the interaction of soil properties and hydrological pathways.

The close interaction of the hydrological cycle with the soil and vegetation of a drainage basin makes the separation of these processes difficult. This chapter describes the hydrological pathways of the upper section of the drainage basin and characterises the physical characteristics of the soil which affect properties such as water retention and hydraulic conductivity. Environmental variables which may help to explain water fluxes such as evapotranspiration and moisture deficits are also discussed.

4.1.0. Hydrological Inputs

The atmosphere supplies water and nutrients to the ground surface and the measurement of these parameters is important in nutrient cycling studies (Ovington, 1965). Bormann and Likens (1969) suggest that 'the terrestrial ecosystem is heavily dependent on precipitation as a source of nutrients'. Therefore the amount, frequency and duration by which precipitation is supplied to an ecosystem is also of considerable importance in understanding solute movements. Figure 4.1 illustrates the total monthly rainfall collected at the meteorological station for the study period, June 1980 to December 1981. The totals for the six months preceding the study period are presented in Table 4.1 with the mean monthly figures for Atherstone Sewage Works (Whitfield and Beard, 1980).

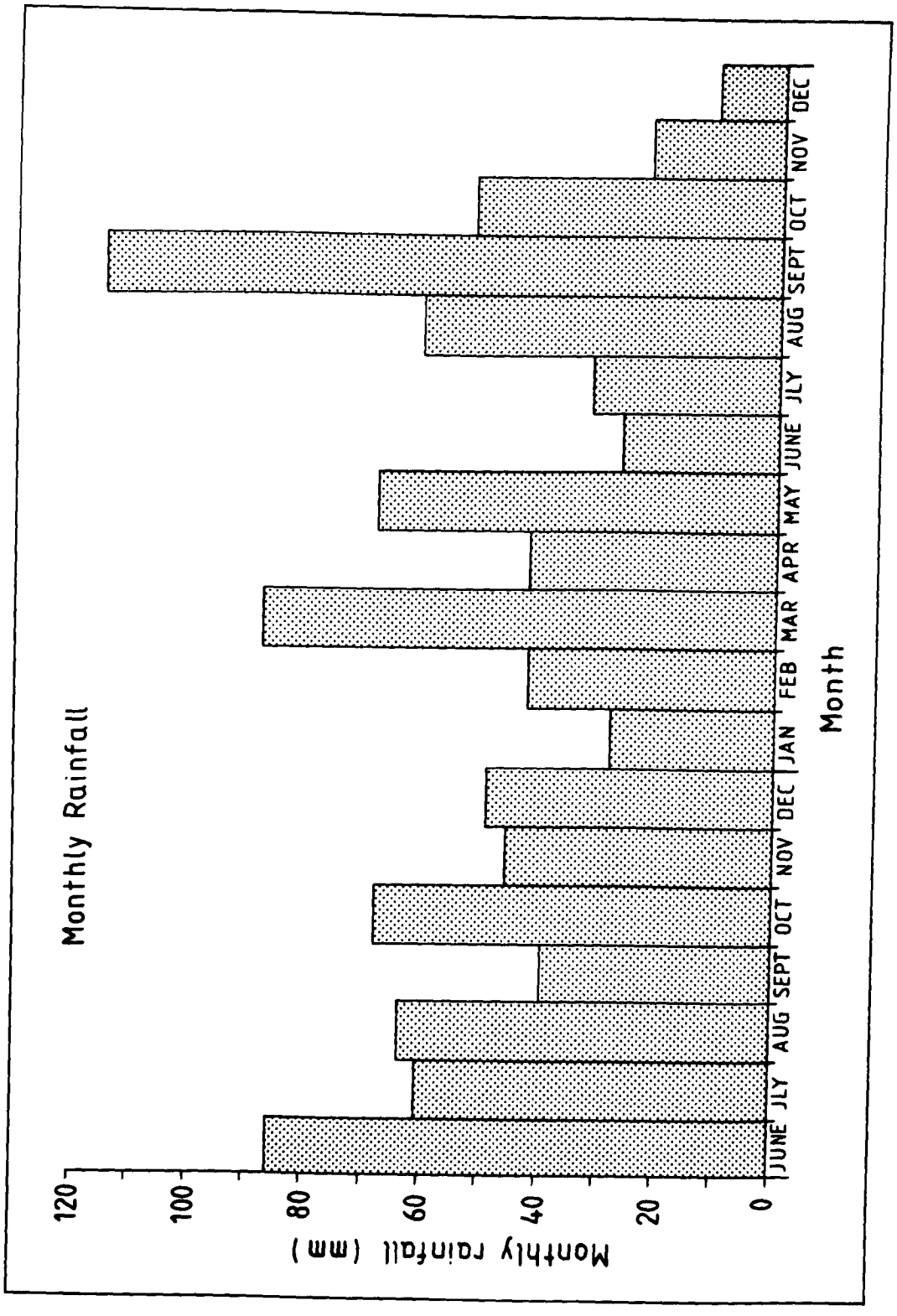


Figure 4.1 Monthly rainfall 1980-1981

Table 4.1 **Monthly rainfall at the study site 1980-1981 and mean monthly rainfall, Atherstone Sewage Works 1941-1970**

Month	Study site monthly totals(mm)		Mean monthly (mm) Atherstone Sewage Works
	1980	1981	1940-1970
January	27.5	28.0	57.0
February	65.5	43.0	45.0
March	35.0	88.0	46.0
April	9.0	43.0	46.0
May	12.0	71.0	57.0
June	86.0	27.0	52.0
July	61.0	32.0	64.0
August	64.0	63.0	71.0
September	39.0	115.0	56.0
October	68.0	53.0	58.0
November	45.0	23.0	65.0
December	49.0	12.0	57.0
Total	561.0	598.0	674.0

The study site catch for 1980 and 1981 is lower than the annual average at the Atherstone Sewage Works. Foster and Grieve (1981) showed that on-site data for this basin during 1978-80 was lower in rainfall catch compared with Birmingham Airport data. The lower than average totals may be due to a rainshadow effect from a small ridge lying to the south-west of the meteorological station. Rainfall in June 1980 (86mm) was greater than average for that month and was due to convective rainfall. Volumes in March (88mm) and September (115.0mm) 1981 are also greater than average for these months and are attributable to the passage of a

series of depressions, identified by the on-site barometric records. Volumes in April (9.0mm) and May (12.0mm) 1980 are unusually low compared to the monthly averages due to a long lived high pressure system. These two months precede the study period but they may have important implications for the interpretation of data for the succeeding months. Figure 4.1 shows the monthly rainfall volumes and indicates that no definite seasonal trend in rainfall patterns occur. The monthly Antecedent Precipitation Index (A.P.I.) is an alternative means of characterising the properties of rainfall and provides a method of evaluating the effect that past rainfall has on present conditions. The relationship of rainfall to time was assumed to be exponential and a constant, K, was employed as a decay function so that past rainfall exerts progressively less influence on the value of the index as time proceeds (Gregory and Walling, 1973). Values of K usually lie between 0.85 and 0.98 depending on the soil and geology of the basin. The lower the value for K the greater the permeability of the soil and underlying rock. A value of 0.90 was estimated for the study basin on the basis of the known soil type and geology.

Equation 4.1

$$Pa = (Pa_{m-1} \cdot K) + P$$ Gregory and Walling (1973)

where Pa_{m-1} = index for preceding month

P = rain in preceding month

Figure 4.2 shows the plotted monthly A.P.I. and illustrates a cumulative increase in the index confirming that there was no seasonal trend in the rainfall distribution. Weekly volumes of rainfall for the study period were highly variable, (102.6% coefficient of variation) ranging from 0 to 55mm, the latter during week ending 12 8 81, whilst the mean weekly volume was

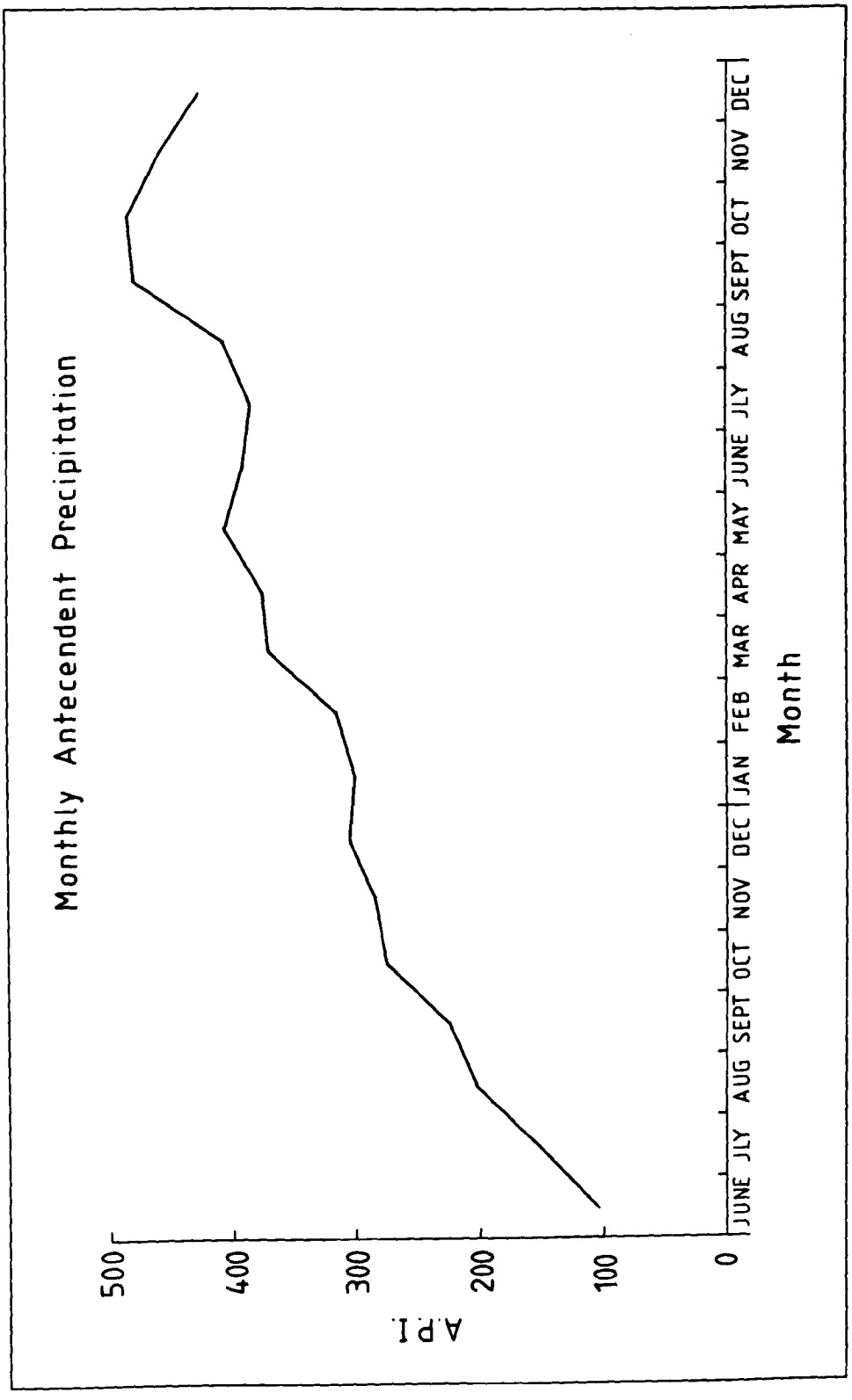


Figure 4.2 Monthly antecedent precipitation index 1980-1981

13.4mm. The maximum rainfall intensity of 3.75mm hr^{-1} was recorded on 19 9 81 but most storms had rainfall intensities of approximately 1.0mm hr^{-1}.

Vegetation in both the growing and dormant seasons acts as a barrier to falling rain, intercepting varying amounts of water according to canopy morphology, leaf type and storm size and intensity. An interception loss of 5-40% is usually expected (Helvey and Patric, 1965) but Eaton (1973) states that between 1-3mm of rain must fall to wet a canopy before throughfall can take place. This storage capacity has important implications for the interpretation of rainwater chemistry. During the study period 10.98% of rainfall was intercepted by the oak canopy and a further 1.36% by the bracken canopy. During the growing season bracken fronds increased interception by a further 4.5%. Table 4.2 provides a more detailed description of interception and weekly variation in catch. Stemflow was not measured in this project and interception values were therefore artificially increased by the inclusion of a water volume which, in reality reached the woodland floor. An estimation of stemflow volume was made using equations reported by Helvey and Patric (1965).

Equation 2

$$S = 0.007P - 0.002 \quad \text{Summer}$$

$$S = 0.017P - 0.002 \quad \text{Winter}$$

where S = stemflow (mm)

P = rainfall for that period (m)

These equations were derived from a study on a 100-120 year old stand of oaks which would have had a similar morphology to those in the present study. Calculation showed that only 12.1mm of the gross precipitation

Table 4.2 **Precipitation characteristics**

	Rainfall	Oak Throughfall	Bracken Throughf
Total input June - Dec. 1980 (mm)	412.0	372.7	368.8
weekly $\bar{x}$ (mm)	13.4	13.3	13.1
% CV	84.4	83.3	84.1
% interception		9.5	10.5
Total input Jan. - Dec. 1981 (mm)	598.0	526.5	516.9
weekly $\bar{x}$ (mm)	11.8	11.0	11.0
% CV	105.1	127.0	126.0
% interception		11.9	13.6

input for the entire study reached the woodland floor as stemflow. This value represents 1.2% which can be deducted from the interception loss values.

Variation in throughfall catch is rarely quoted by authors and no conclusion about the precision of experiments can be made. Helvey and Patric (1965) state that if the percentage coefficient of variation between gauges is plotted for each storm event, a conclusion on the precision of the gauges can be drawn. The data for the throughfall gauges in this study showed that the majority of coefficients of variation were less than 50% and there was no significant difference in the variation between small and large storm events at the 95% level. The students T test was performed on the percentage coefficient of variation in catch between 22 summer and winter observations and again no significant difference in the data set was found. These results indicated that gauge size and number was sufficient to minimise the potential spatial variations in catch caused by the canopy structure, season and storm size.

4.1.1. Litter Interception and Infiltration

In a forest ecosystem, precipitation can be further intercepted by litter on the soil surface. A litter layer has its own moisture holding capacity which depends on the type of vegetation, litter depth, microclimate and biological activity within the litter (Helvey and Patric, 1965). As much as 40% of precipitation can be intercepted in an individual storm though on an annual basis approximately 2.5% will be intercepted and evaporated from the litter surface in an upland oak forest (Blow, 1955). Interception by the litter layer is usually greater in winter as the vegetation canopy preferentially intercepts in summer. Figure 4.3A illustrates the moisture content of the sampled litter as a percentage of dry weight. The graph

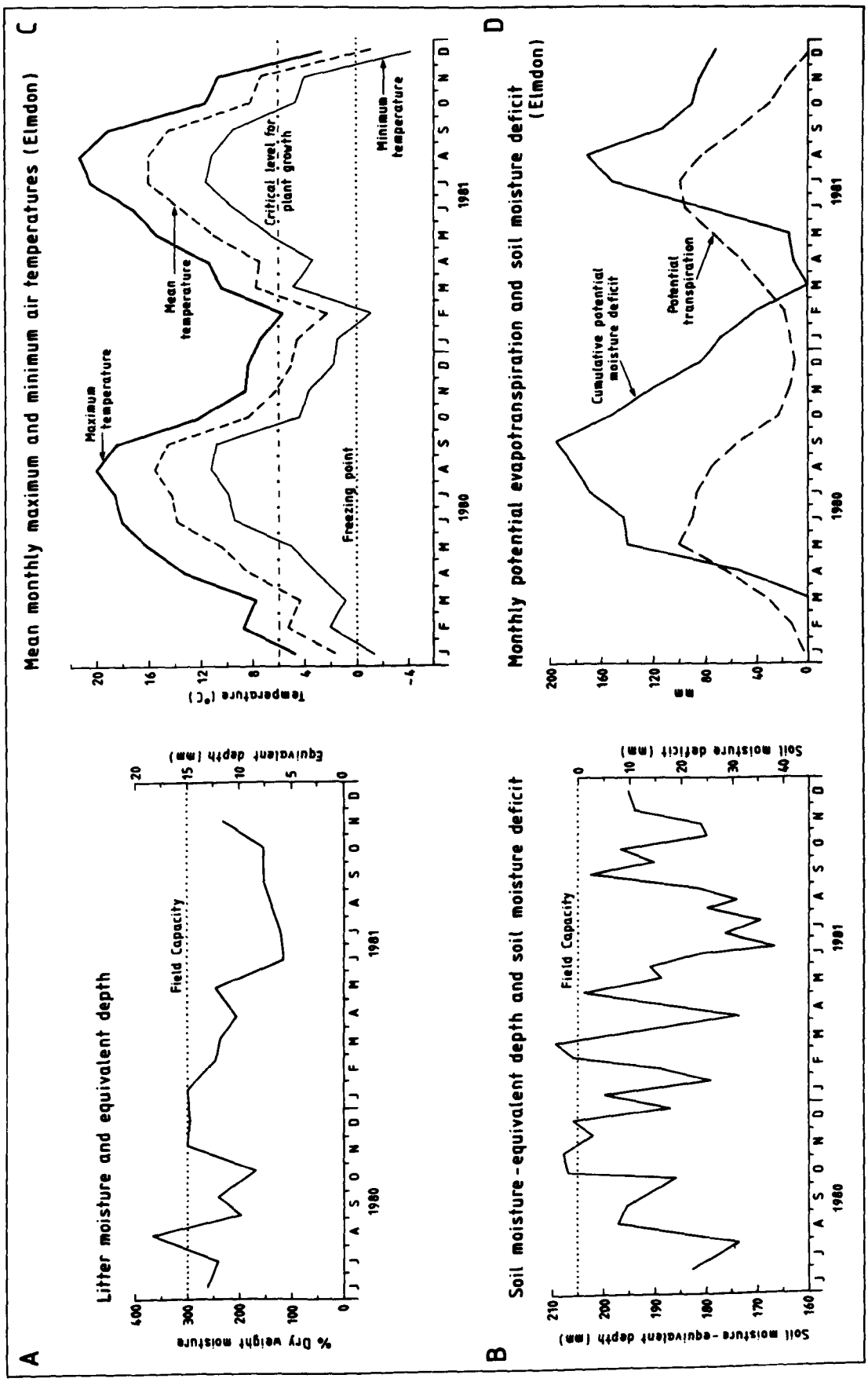

A
Litter moisture and equivalent depth
% Dry weight moisture
Equivalent depth (mm)
Field Capacity
J J A S O N D J F M A M J J A S O N D
1980
1981
B
Soil moisture-equivalent depth and soil moisture deficit
Soil moisture-equivalent depth (mm)
Soil moisture deficit (mm)
Field Capacity
J J A S O N D J F M A M J J A S O N D
1980
1981
C
Mean monthly maximum and minimum air temperatures (Elmdon)
Temperature (°C)
Maximum temperature
Mean temperature
Critical level for plant growth
Freezing point
Minimum temperature
J F M A M J J A S O N D J F M A M J J A S O N D
1980
1981
D
Monthly potential evapotranspiration and soil moisture deficit (Elmdon)
mm
Cumulative potential moisture deficit
Potential transpiration
J F M A M J J A S O N D J F M A M J J A S O N D
1980
1981

Figure 4.3

shows a summer trough in 1981 with a minimum value of 107% in June, whilst winter values range from 200-300%. The moisture content was also expressed in terms of equivalent depth of the litter layer, using a calculated mean bulk density value of 0.05g cm^{-3} and average litter depth of 10cm. Field capacity was estimated to occur at 15mm equivalent depth or 300% dry weight and Figure 4.3A shows the calculated moisture deficit which occurred during the summer. During 1981 approximately 21% of incident precipitation was initially intercepted by the litter layer thus emphasising its importance as a water storage zone. After a rainfall event more than half of the litter moisture is lost by percolation and evaporation within the first three days (Blow, 1955). The litter has several important functions in the hydrological cycle, first it absorbs the impact of falling raindrops and thus protects the soil from erosion, secondly the litter acts as a mulch on the soil surface, retaining water by minimising evaporation from the soil and finally the low bulk density of litter increases the infiltration capacity of the woodland floor.

Infiltration is the process by which precipitation enters the soil and the amount and final rate of infiltration is an important measurement in the investigation of solute pathways. The infiltration characteristics of a soil vary with soil type and depth, land use, topography, antecedent moisture conditions, vegetation and litter and type, the moisture deficit and the volume and intensity of precipitation. The entry of water into the soil down the hillslope is shown in Figure 4.4 in the form of infiltration curves measured on 11 3 81. Infiltration commenced at a very high rate until the litter layer became saturated. The decrease in the initial infiltration rate was mainly due to the reduction of the matric suction gradient which occurred as the wetting front of the infiltrating water moved down the soil. Eventually a constant rate was attained which represented the

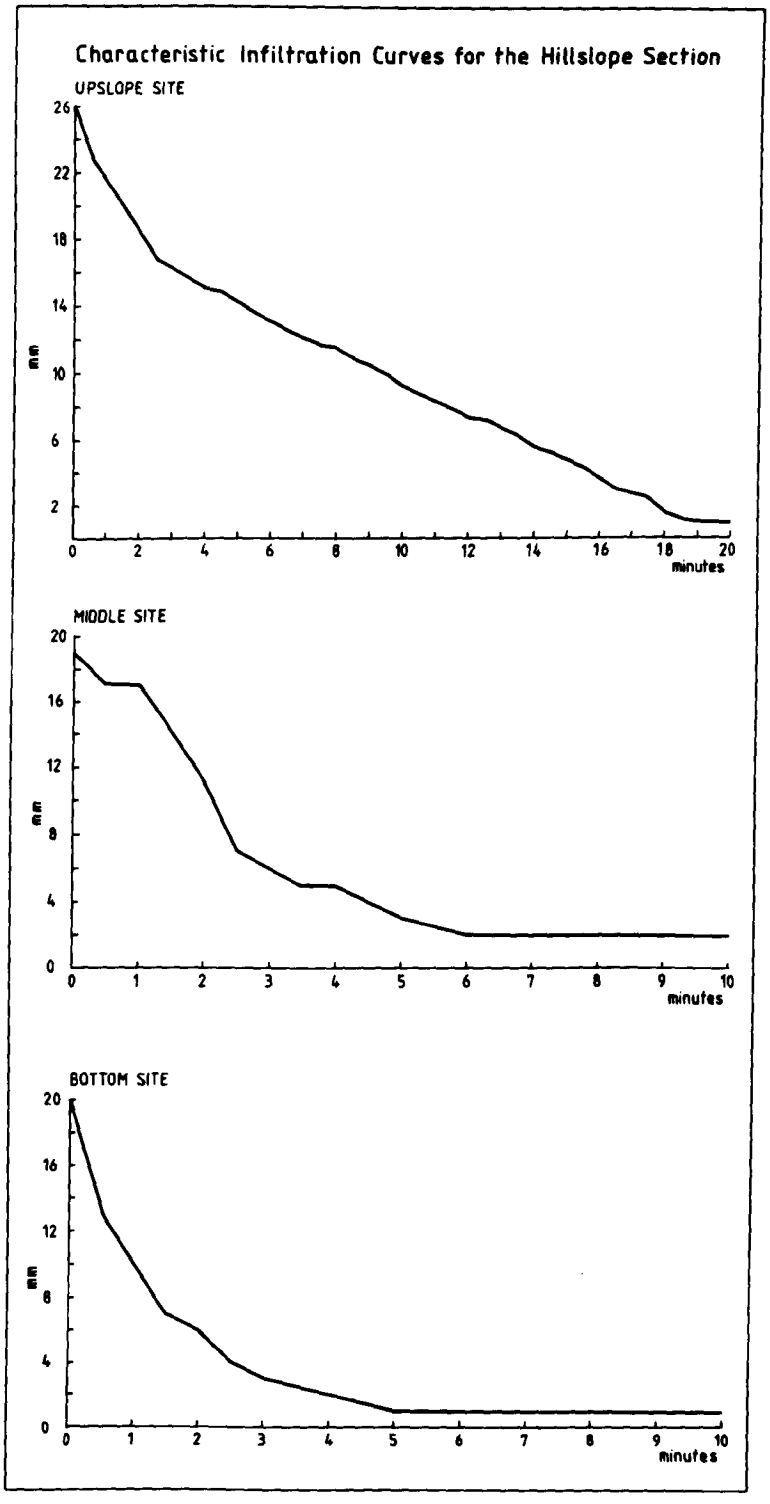

Characteristic Infiltration Curves for the Hillslope Section
UPSLOPE SITE
mm
minutes
MIDDLE SITE
mm
minutes
BOTTOM SITE
mm
minutes

Figure 4.4

infiltration capacity of the soil; 1.13, 2.0 and 0.98 mm min^{-1} at the three sites on the hillslope. The relatively smooth decline of each curve demonstrates the uniformity of the soil profile. However, the middle and bottom sites attain infiltration capacity within a few minutes and Table 4.3 illustrates the importance of antecedent soil moisture conditions and the proximity of the water table in explaining infiltration characteristics.

Table 4.3 **Soil moisture characteristics during infiltration test**

Site	Horizon			Water table
	Ah	Bt(g)	BCg	depth
Upslope	46.9	23.0	20.5	3000mm
Middle	48.0	27.2	28.6	650mm
Bottom	49.4	28.5	30.2	180mm

Soil in the phreatic zone had a zero or positive matric moisture potential, consequently, as infiltrating water moved down the soil profile the matric suction gradient was reduced. At the middle and bottom of the hillslope, the water table lay near the soil surface and therefore profile saturation and infiltration capacity were quickly reached. Antecedent soil moisture conditions were near field capacity and little infiltrating was required to wet the profile. Infiltration capacity was therefore attained relatively quickly. Infiltration rates at the middle and bottom hillslope sites are clearly affected by soil moisture and the proximity of the water table. The final infiltration rate was thus determined by the underlying clay drift which probably had a lower hydraulic conductivity than the overlying sandy loam (Baver et al, 1972). These final infiltration rates (67.8, 120.0, 58.8mm hr^{-1}) can be compared with the maximum rainfall intensity which

occurred (3.75mm hr^{-1}) indicating it is unlikely that the infiltration capacity of this soil was reached in any storm event. The high capacity is probably due to the retention of moisture in the litter layer and the coarse sandy loam texture of the topsoil. In this experiment no correction factor was employed for lateral flow from the flooding ring (Hills, 1971) and this may also partially account for the high capacities measured. Typical infiltration capacities for a soil with a sandy loam texture are 20-25mm hr^{-1} (Gregory and Walling, 1973) and 10-20mm hr^{-1} (Hillel, 1971).

Infiltration tests which were performed in the summer provided similar results for the final infiltration capacity, 1.21, 1.86, 0.71mm min^{-1} for the respective downslope sites. The main difference was the length of time which was required to attain the final rate. This was due to the drier antecedent moisture conditions of the litter and soil on the hillslope.

4.2.0. The Soil

The Melbourne soil series identified on the hillslope comprised a coarse loamy gleyic brown earth underlain by Carboniferous sandstone. It was distinguished from the closely associated Rivington series by the presence of mottles within 80cm. Typical deciduous woodland L, F and H horizons overlaid a thin, brown, humose, sandy loam A horizon which was weakly structured. The A horizon was underlain by a brown, moderately developed, slightly mottled, clay loam Bt(g) horizon which contained illuvial concentrations of clay. This horizon merged with a yellowish brown, massive, gleyed sand loam BCg horizon. The soil was underlain by interbedded unconsolidated parent material, Cu, which included clay, stony, silty clay and sandy loam layers superimposed on the Carboniferous sandstone. Table 4.4 provides a full representative profile description and

Table 4.4 **Representative Profile Description**

Profile:	Melbourne Date: 15 7 81
Location:	Monks Park Wood, Atherstone (G.R. 292,961)
Elevation:	125 O.D. Slope and Aspect: 6^{0} concave
Land Use:	Oak woodland, understorey of bracken
Horizons: cm	
0 - 6 L and F	Bracken and oak litter over partly decomposed bracken and oak litter; many fine bracken roots; abrupt wavy boundary.
6 - 10 H	Black (5YR 2.5/1) amorphous organic material; many fine fibrous bracken roots and many coarse fleshy rhizomes; abrupt smoth boundary.
10 - 16 Ah	Dark reddish brown (5YR 2.5/2) sandy loam, moist; weakly developed subangular blocky; medium packing density; very porous; very fine fissures; slightly sticky; non-plastic; abundant fine fibrous bracken and oak roots and many coarse fleshy rhizomes; no earthworms; sharp smooth boundary.
16 - 55 Bt(g)	Strong brown (7.5YR 5/8) clay loam with few fine and medium distinct clear dark brown (7.5 YR 4/2) and dark greyish brown (10YR 4/2) mottles; occasional small, medium and large angular sandstone and limestone fragments; moderately developed blocky; moist; low packing density; very porous; very fine fissures; moderately weak ped strength; non-sticky; non-plastic; few fine and medium oak roots; clear wavy boundary.
56 - 140 BCg	Yellowish brown (10YR 5/4) sandy loam with common medium distinct clear dark greyish brown mottles (10YR 4/2) slightly moist; massive; apedal; slightly stony; small, medium and large angular fragments; very porous; moderately weak soil strength; non-sticky; non-plastic; few coarse woody oak roots, abrupt smooth boundary.
140+ Cu	Interbedded unconsolidated parent material. Grey clay over very stony sandy loam and silty clay underlain by an exremely stony layer over further grey silty clay at 340cm.

Figure 4.5 illustrates the soil profile. The Bardsey soil series, a cambic stagnogley, was found at the base of the hillslope. This soil is defined as a fine loamy over clayey soil and was derived from local drift over clay or silty shale. The Bardsey soil type and other stagnogley soils are found in the drainage basin on drift deposits between the more resistant sandstone ridges. Full profile descriptions of the Bardsey series and other gley soils in the basin are provided by Whitfield and Beard (1980).

4.2.1 Soil Moisture

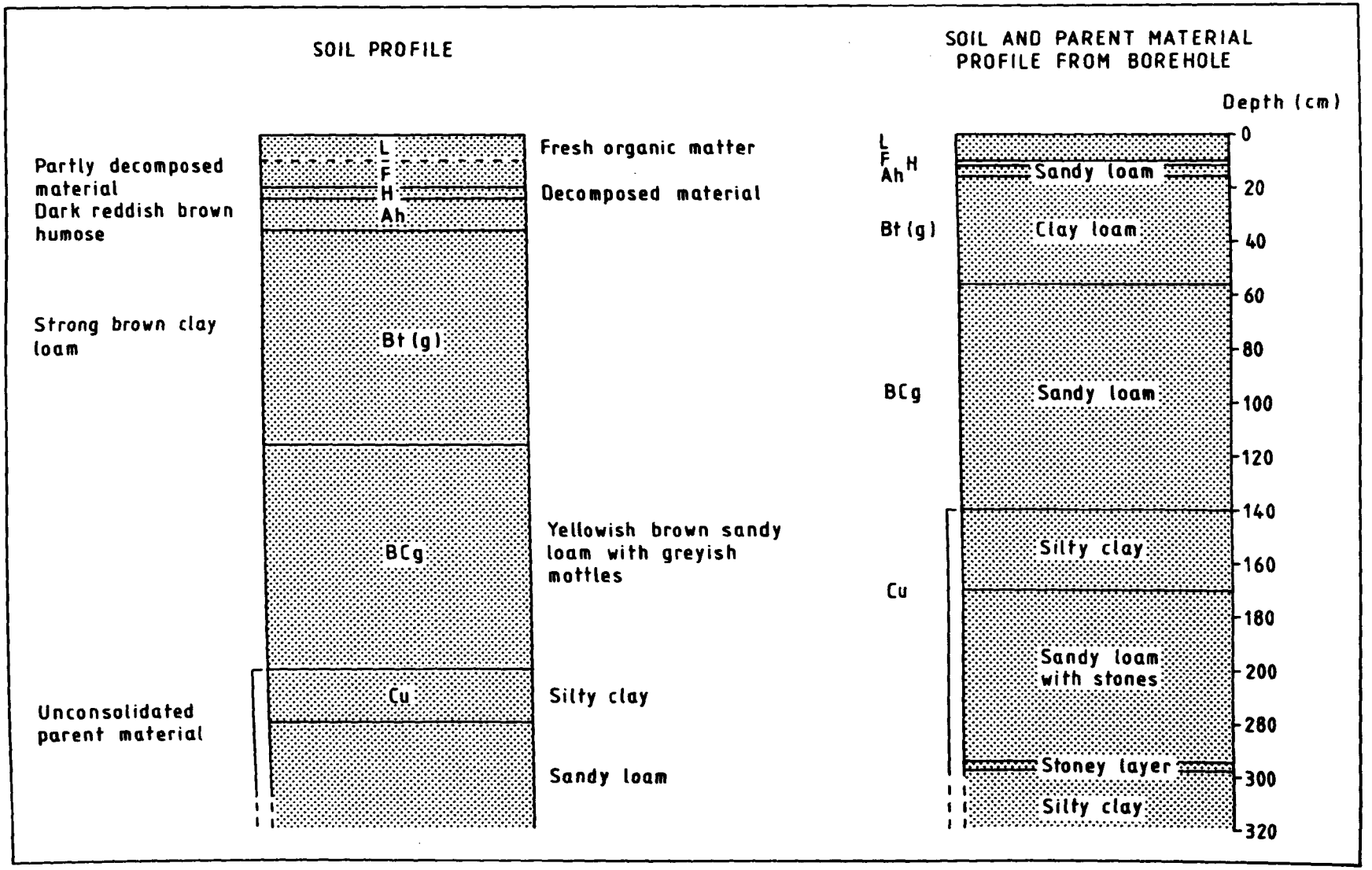
Soil texture greatly influences the water retaining properties of a soil profile and hence the growth of plants (Black, 1968). Gupta and Larson (1979) state that soil water retention measurements are needed to describe the availability of soil water to plants and to model the movement of water and solutes in an unsaturated soil. Thus it is important to recognise the porosity and suctions which are in operation since these factors decide the amount of water remaining in the soil.

Table 4.5 illustrates the percentages of clay, silt and fine, medium and coarse sand for each soil horizon and the 140 and 310cm depths. The Ah and Bt(g) horizons were classified as a sandy loam and clay loam respectively but they may have similar characteristics due to their proximity on the textural triangle (Hodgson, 1974). The majority of sand in these two horizons is fine and therefore water retaining properties may be improved by this type of sand fraction. Clay content increases in the Bt(g) profile and indicates translocation of clay minerals from the Ah horizon. Bulk density is low for a soil of this textural type and in the Ah horizon is probably reduced by the presence of organic matter. Density values normally increase in the subsoil with the absence of significant quantities of organic matter. However, the increase in clay content in the Bt(g) horizon may account for its lower density. Total pore space of each soil horizon was estimated from the following equation:

Table 4.5 **Summary of soil physical properties**

Horizon	Ah	Bt(g)	BCg	Cu	
Depth (cm)	10-16	16-56	56-140	140	310
Bulk Density (g cm^{-3})	1.246	1.217			
mean moisture content % dry wt	45.2	21.7			
% by volume of all pores	54.0	55.1			
Sand 600um - 2mm	2.12	1.62	1.36	7.27	1.15
200 - 600um	14.84	16.19	27.15	2.51	0.83
60 - 200um	43.63	30.04	28.87	2.72	1.22
Silt 2 - 60um	21.71	32.8	29.79	42.89	49.24
Clay 2um	17.70	19.35	12.83	44.61	47.56
Texture	sandy loam	clay loam	sandy loam	clay	silty clay

Figure 4.5


SOIL PROFILE
Partly decomposed material
Dark reddish brown humose
Strong brown clay loam
Unconsolidated parent material
L
F
H
Ah
Bt(g)
BCg
Cu
Fresh organic matter
Decomposed material
Yellowish brown sandy loam with greyish mottles
Silty clay
Sandy loam
SOIL AND PARENT MATERIAL PROFILE FROM BOREHOLE
Depth (cm)
L
F
Ah
H
Bt(g)
BCg
Cu
Sandy loam
Clay loam
Sandy loam
Silty clay
Sandy loam with stones
Stoney layer
Silty clay
0
20
40
60
80
100
120
140
160
180
200
280
300
320

Equation 4.3

$$T\% = \left(1 - \frac{Db}{Dp}\right) \times 100 \qquad \text{(Hall } \underline{\text{et al}}\text{, 1977)}$$

where Db = Bulk density

Dp = Particle density

T% = Total pore space

assuming a Dp of 2.4g cm^{-3} for the topsoil and 2.65g cm^{-3} for the subsoil. The figures in Table 4.5 indicate a soil with a total porosity similar to the average soil porosity of 50% quoted by Baver et al (1972). Pore space is inversely related to bulk density (Hall et al, 1977) thus explaining the slightly larger porosity in the Bt(g) horizon.

Moisture retention properties were calculated using the regression equations provided by Hall et al (1977), which are based on particle size, bulk density and organic carbon contents. Up to 83% of variance in moisture retention properties is explained in the equations by these parameters. Table 4.6 shows the calculated moisture retention as a percentage of volume for 0.05, 0.10, 0.4, 2 and 15 bar suctions of the study site soil. Available water (Av) in the Bt(g) is moderately small according to the Soil Survey classification (Whitfield and Beard, 1980). This is due to the fairly large amount of unavailable water which is retained by clay particles at suctions greater than 15 bar. Available water in the Ah horizon is moderately large (Whitfield and Beard, 1980), due to retention by organic matter and the coarser soil texture. Table 4.6 also gives the estimated air capacities (C) which indicate the amount of coarse pores (greater than 60um) in the soil horizons.

Table 4.6 **Moisture Retention Properties of Ah and Bt(g) horizons (Hall et al, 1977)**

				Bars				
	T%	Av	C	0.05	0.10	0.40	2.0	15.0
Ah	48	19.2	10.2	37.8	35.1	30.4	23.5	15.9
Bt(g)	54	14.7	19.5	34.5	31.5	28.0	21.7	19.8

Av = @0.05 - @15.0

C = T% - @0.05

Total porosity in the Ah (54.0%) and Bt(g) (55.1%) horizons is average for soils of this type but it is the pore size distribution which determines soil water residence times and the type of soil water flow within the soil. At field capacity (0.05 bar/5cm H_2O) as defined by Webster and Beckett (1972) and Hall et al (1977), all soil pores greater than 60um will have drained of soil water and an estimate of the amount of macropores can be made. Tensiometer data for this site showed field capacity values to be approximately 4cm H_2O in the A horizon and 7cm H_2O in the Bt(g) horizon. The volumetric soil moisture content in the Ah and Bt(g) horizons at field capacity was 43.6% and 18.9% respectively. From total porosity figures it was estimated that 10.4% and 36.2% of pores in the Ah and Bt(g) horizons were greater than 60um and could be defined as macropores. The percentage of macropores is equivalent to the estimated air capacity figures in Table 4.6 The A horizon value is directly comparable, but the Bt(g) horizon shows a much larger air capacity than in Table 4.6 and the moisture content of the Bt(g) horizon at field capacity was low compared with other clay loam subsoils (Hall et al, 1977). It is possible that this horizon contains additional macropores created by roots and rhizomes, pipes (Jones, 1971), fissures and planar voids between interpedal faces (Scotter, 1978) thus increasing aeration. The low moisture contents certainly suggest a freely draining soil with little water retention, despite the increased clay content.

The relative importance of soil water flow in macropores has not been fully appreciated in the past, but Thomas and Phillips (1979) present evidence to show that flow of water through macropores is important in soil and groundwater recharge and in salt movement through soils. In a soil with macropores, infiltrating water need not necessarily displace resident soil water but can move via macropores without significantly

raising the moisture content, consequently the water-table may begin to rise long before field capacity is reached. Scotter (1978) states that continuity of voids is as important as pore radius and volume, whilst Bouma and Anderson (1977) show that nearly all soil water flow occurs in a few large channels despite their relatively minor contribution to total soil porosity. The final rate of infiltration is comparable to the vertical, saturated hydraulic conductivity (Anderson and Burt, 1978b). Extremely porous soils exhibit high values of saturated hydraulic conductivity and the large infiltration capacities down the hillslope (1.13, 2.0, 0.98mm min^{-1}) confirm the relationship for this soil.

Soil water which is resident in fine pores (<60um) will only be displaced on a significant scale, when the soil matrix becomes saturated. This pattern of water movement was observed by Nortcliff and Thornes (1978) in a tropical rainforest where the 'by pass' mechanism of water movement operated and smaller pore spaces were only flushed when soil saturation was approached. Table 4.6 shows that as soil moisture tension increases the volumetric moisture content decreases, indicating progressive emptying of finer pore spaces. Figure 4.3B showed that little variation in moisture content occurred over the study period and consequently moisture tensions greater than 1000cm water (1 bar) were not experienced. Tensions greater than 1000cm water would have drained pores with a diameter 30um.

In hydrological studies where moisture storage and fluxes are considered it is convenient to express soil moisture in terms of equivalent depth. The calculation takes into account variation in bulk density down the soil profile and identifies the water storage capacity of the soil (Curtis et al, 1976). Figure 4.3B shows moisture content in terms of the equivalent

depth of water in a soil of 0.75m depth (Hodgson, 1974). A maximum storage of 209mm occurs in winter with minimum values occurring in summer. The assumption of a winter field capacity of 205mm storage in the profile (Figure 4.3B) enabled calculation of moisture deficits in the soil. The moisture deficit at winter field capacity was assumed to be zero. Subsequent values of soil water storage less than 205mm were assumed to exhibit a moisture deficit.

Figure 4.3B shows a maximum soil moisture deficit (S.M.D.) of 38.2mm in July 1981. It is noticeable that the soil nearly returned to field capacity in May 1981 when a greater than average rainfall (71.0mm) replenished soil moisture. In general field capacity was reached in November and the deficit commenced in April. The S.M.D. was a seasonal phenomena and was largely controlled by evapotranspiration. Figures 4.3C and 4.3D show maximum and minimum air temperatures, potential evapotranspiration and potential cumulative soil moisture deficit at Birmingham airport for 1980-1981. The measured S.M.D. is far less than the potential S.M.D., the latter being calculated for open grassland with a continuous water supply and this illustrates the importance of using actual S.M.D. data. The low values at Atherstone may be attributable to the continued high rainfall in summer and the thick litter layer minimising soil moisture loss. In addition transpiration by vegetation in the drainage basin does not commence until May, thus reducing the actual evapotranspiration. Evapotranspiration and the water balance of the catchment are discussed in section 4.5.0. In a deciduous forest the majority of evaporation is usually attributable to tree activity but the contribution of the understorey vegetation is commonly ignored. Roberts et al (1980) found that water loss from a bracken canopy can be appreciable and in excess of 65% of the total woodland budget. In summer the transpiration rates of shallow

rooting plants is usually decreased due to a reduction in the amount of easily available water. In this woodland the moisture deficit was low (Hodgson, 1974) and maximum soil tensions did not exceed 800cm of water in the Ah horizon. Easily available water is defined by Hall et al (1977) as that water which is held in the soil at tensions of less than 2 bar (2040cm water).

4.2.2. Flow within the Soil

The redistribution of moisture following infiltration can occur vertically or laterally by percolation and throughflow respectively. The movement of soil water is complex and largely depends on antecedent soil moisture conditions and forces such as gravity and suction which operate within the soil. The use of automated tensiometry, throughflow pits and dye tracing experiments has provided the data necessary to establish a three dimensional flow pattern of soil water movement over time.

Soil water fluxes are best portrayed by an examination of a significant storm event and Figure 4.6 illustrates the six hourly rainfall events from 15 10 80 to 28 10 80. A total of 30.0mm of rain fell on the 16th and 17th October with only a small volume falling in the following 11 days. The progressively smaller influence that this storm had on soil moisture conditions is shown in the six hourly A.P.I. in Figure 4.7. On 16 10 80 at 06.22 hours soil water potentials were negative at all points down the hillslope with lower horizons under the greatest suction (Figure 4.8). By 10.30 hours water potentials were considerably reduced, and at all 15cm depths positive potentials were recorded. At the bottom of the slope positive potentials were recorded for both 15 and 30cm depths (no results for 70cm). Saturated conditions did not persist in the surface horizon as water held in large pores, greater than 60um, drained very quickly in

Figure 4.6

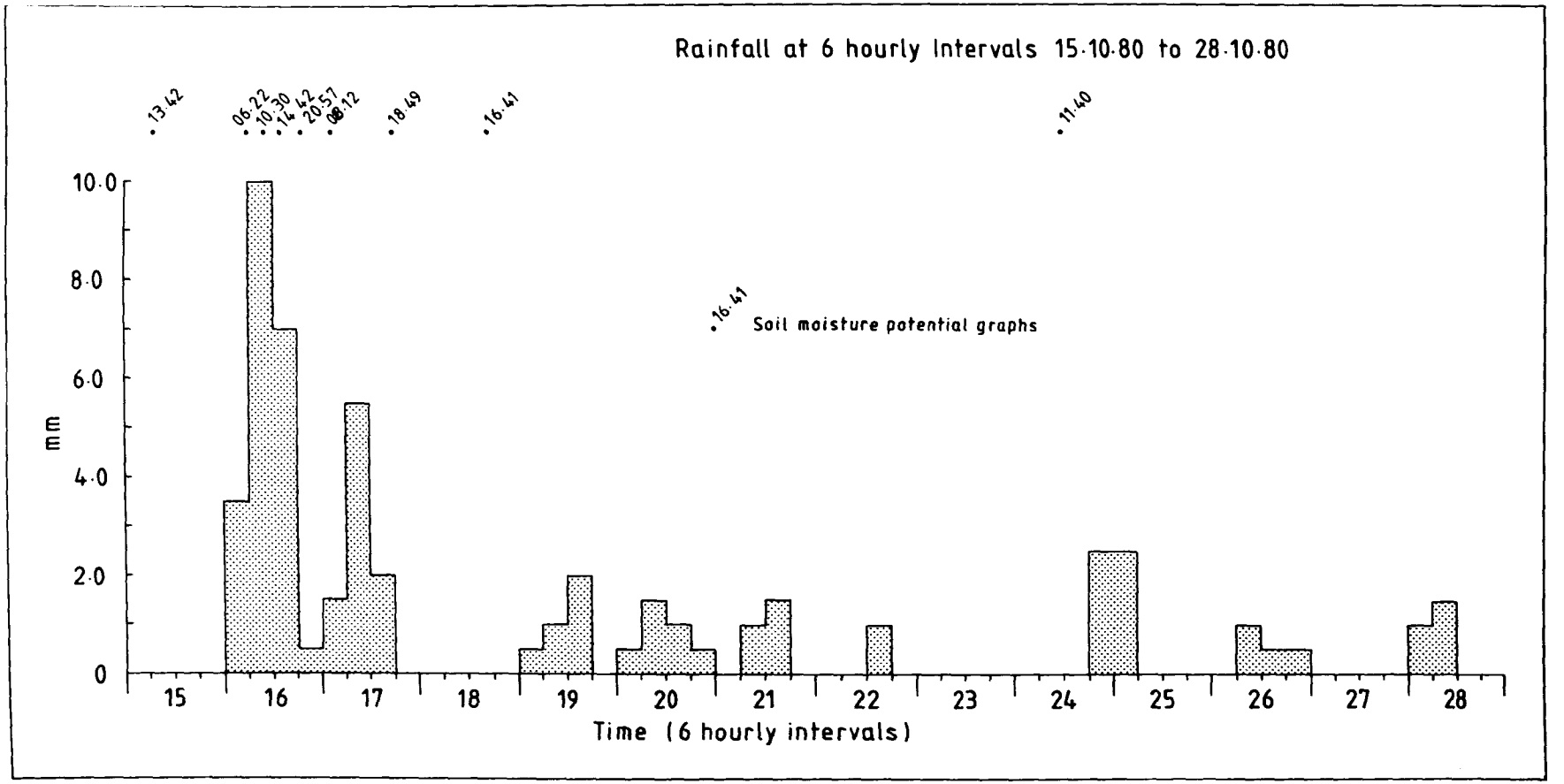
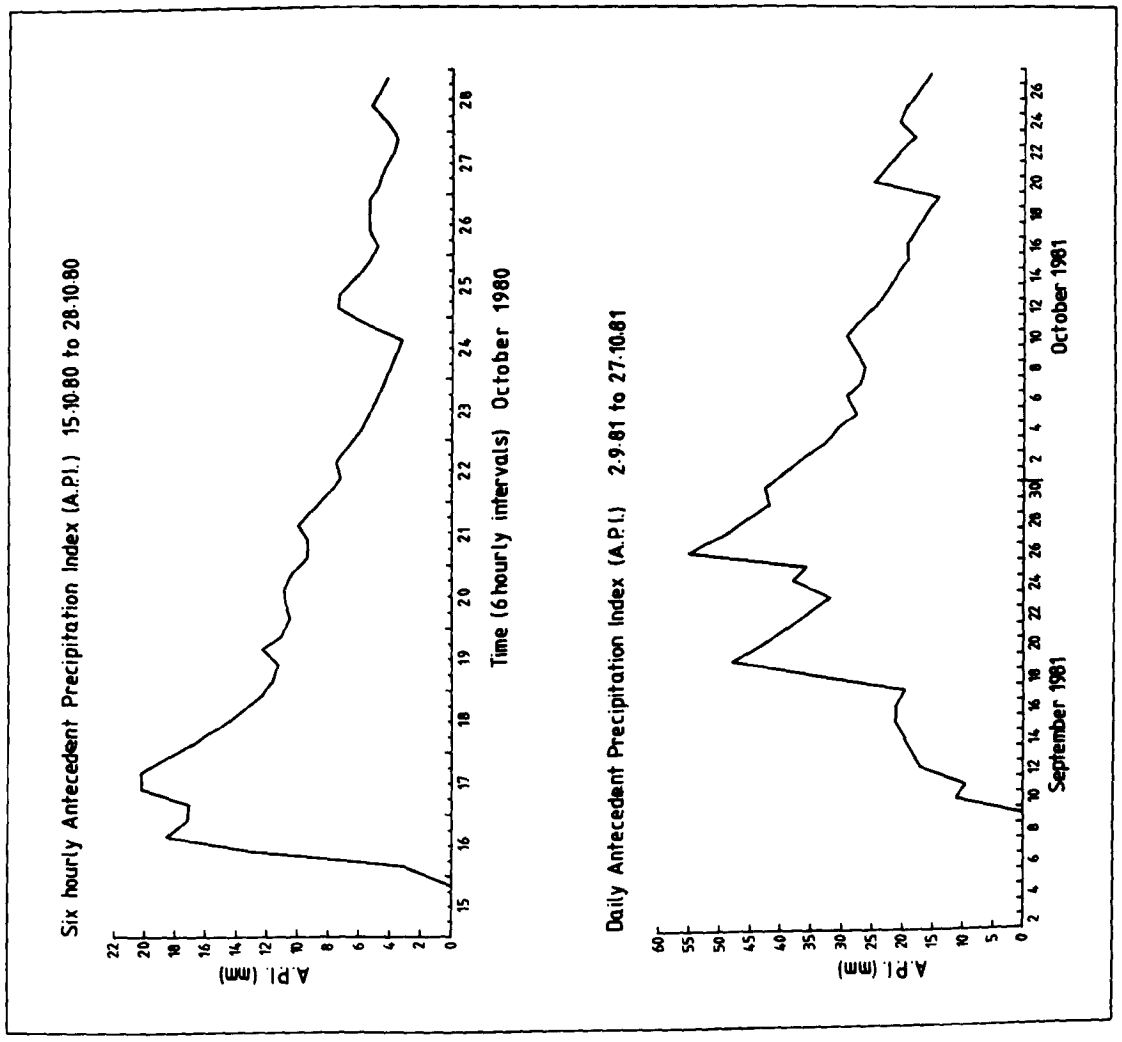

Rainfall at 6 hourly Intervals 15·10·80 to 28·10·80
13.42
06.22
10.30
14.42
20.57
08.12
18.49
16.41
11.40
16.41
Soil moisture potential graphs
10·0
8·0
6·0
4·0
2·0
0
mm
15
16
17
18
19
20
21
22
23
24
25
26
27
28
Time (6 hourly intervals)

Figure 4.7


Six hourly Antecedent Precipitation Index (A.P.I.) 15.10.80 to 28.10.80
A.P.I. (mm)
Time (6 hourly intervals) October 1980
Daily Antecedent Precipitation Index (A.P.I.) 2.9.81 to 27.10.81
A.P.I. (mm)
September 1981
October 1981

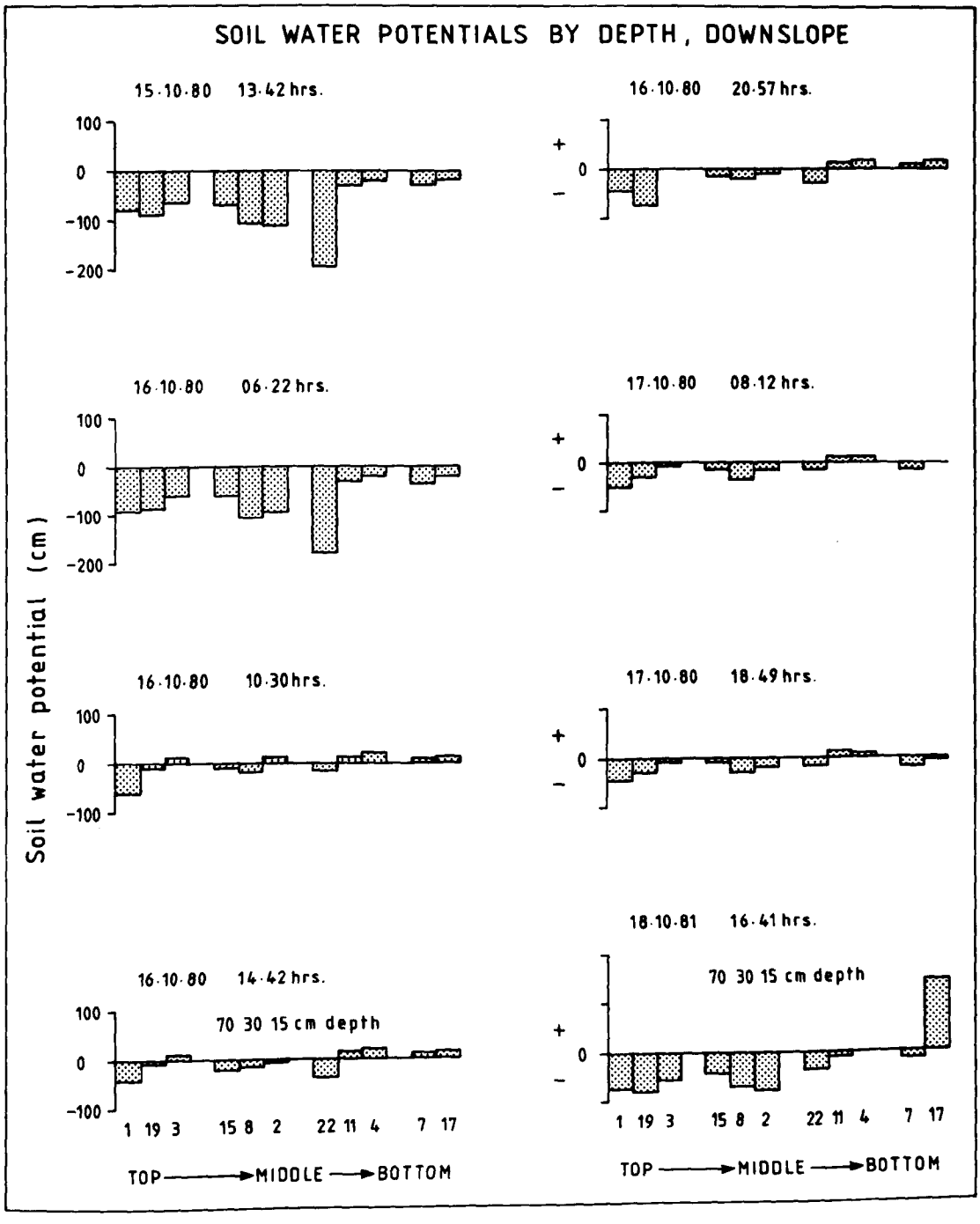

SOIL WATER POTENTIALS BY DEPTH, DOWNSLOPE
15·10·80 13·42 hrs.
16·10·80 20·57 hrs.
16·10·80 06·22 hrs.
17·10·80 08·12 hrs.
16·10·80 10·30 hrs.
17·10·80 18·49 hrs.
16·10·80 14·42 hrs.
18·10·81 16·41 hrs.
70 30 15 cm depth
Soil water potential (cm)
100
0
-100
-200
+
0
−
1 19 3 15 8 2 22 11 4 7 17
TOP → MIDDLE → BOTTOM

Figure 4.8

response to gravity and also to the suction gradients. In a sandy textured, free draining soil, water redistribution is accomplished within two to three days (Hillel, 1971) and Figure 4.8 shows that for this soil the pre-rainfall tensions are attained within two days of the rainfall event. The soil water potentials on the freely draining top and middle sections of the slope reach field capacity at tensions ranging from 40 to 80cm water (0.04 to 0.08 bar) which is in agreement with the field capacity values proposed by Webster and Beckett (1972). An impermeable clay layer underlies the lower section of the slope and soil water is not able to percolate freely, consequently a perched water-table develops in this area and its extent and depth can be identified by the positive potentials which are recorded. The rate at which the downward movement of water occurs is dependent on the hydraulic conductivity of the soil and in saturated conditions a maximum and generally constant rate will prevail (Hillel, 1971). In the unsaturated zone most of the larger pores are empty and thus conductance was low obeying Poiseuilles Law, where 'the total flow rate of water through a capillary tube is proportional to the fourth power of the radius, while the flow rate per unit cross-sectional area of the tube is proportional to the square of the radius' (Hillel, 1971). For example, a 1mm radius pore will conduct a volume as would 10,000 pores of radius 0.1mm. Thus as soil water tension increases a steep drop in hydraulic conductivity occurs and then very steep suction gradients or long periods of time are required for appreciable flow to occur (Hillel, 1971). Table 4.7 illustrates the results from the percolation of Lissamine FF and calculated unsaturated hydraulic conductivity after a five week period (30 9 81 to 11 11 81) and 55mm rainfall.

Table 4.7 **Characteristics of dye percolation in unsaturated soil from 30 9 81 to 11 11 81**

	Hillslope site		
	Top	Middle	Bottom
Lateral flow	0.0	0.0	0.0
General depth cm	25.0	21.0	16.0
Maximum depth cm	30.0	28.0	18.0
Unsaturated hydraulic conductivity ($mm\ min^{-1}$)	0.050	0.046	0.030

The saturated hydraulic conductivity can be inferred from the final rate of infiltration in a saturated soil (Anderson and Burt, 1978b) and as section 4.1.1 shows these are equivalent to 1.13, 2.0, 0.98 mm min^{-1} for the top, middle and bottom sections of the slope respectively. Comparison of the unsaturated and saturated hydraulic conductivity figures emphasises that significant subsurface flow would have only occurred when the soil was saturated.

During a storm event the vertical flux of water dominates but as infiltration ceases the main process is that of lateral throughflow which occurs at all depths but may concentrate above a less permeable horizon (Chorley, 1978). Figures 4.9 and 4.10 represent the plotted soil moisture potentials for 15 and 30cm depths across the tensiometer network for the storm period under consideration. On this shallow slope (6^{o}) the influence of soil water potential is greater than the elevation potential and flow pathways of soil water can be inferred by the construction of flow lines which are orthogonal to the lines of equal soil moisture potential. The graphs illustrate the development of a saturated area, at 15 and 30cm depths, by 10.30 hours on 16 10 80 which extends upslope. As time

Figure 4.9

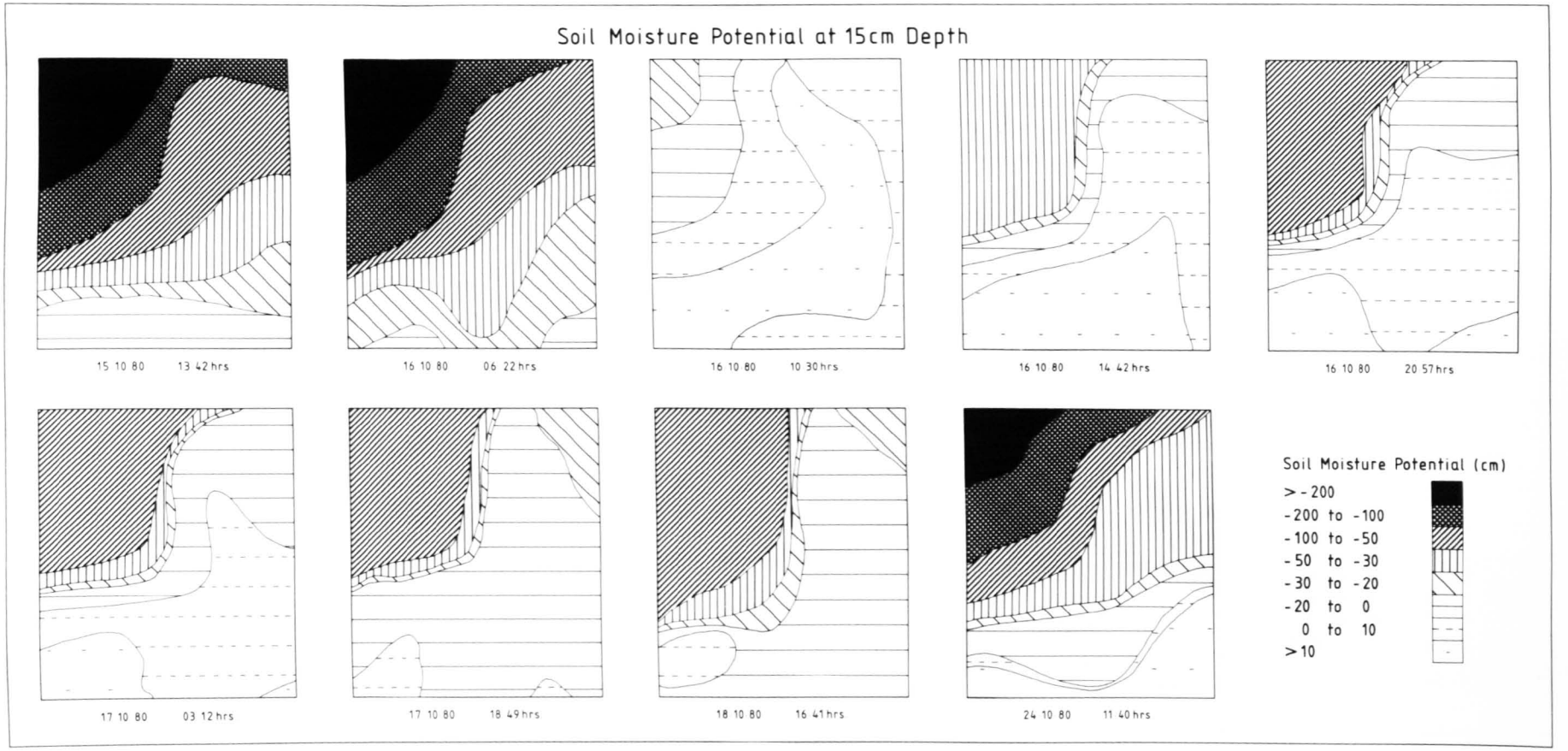
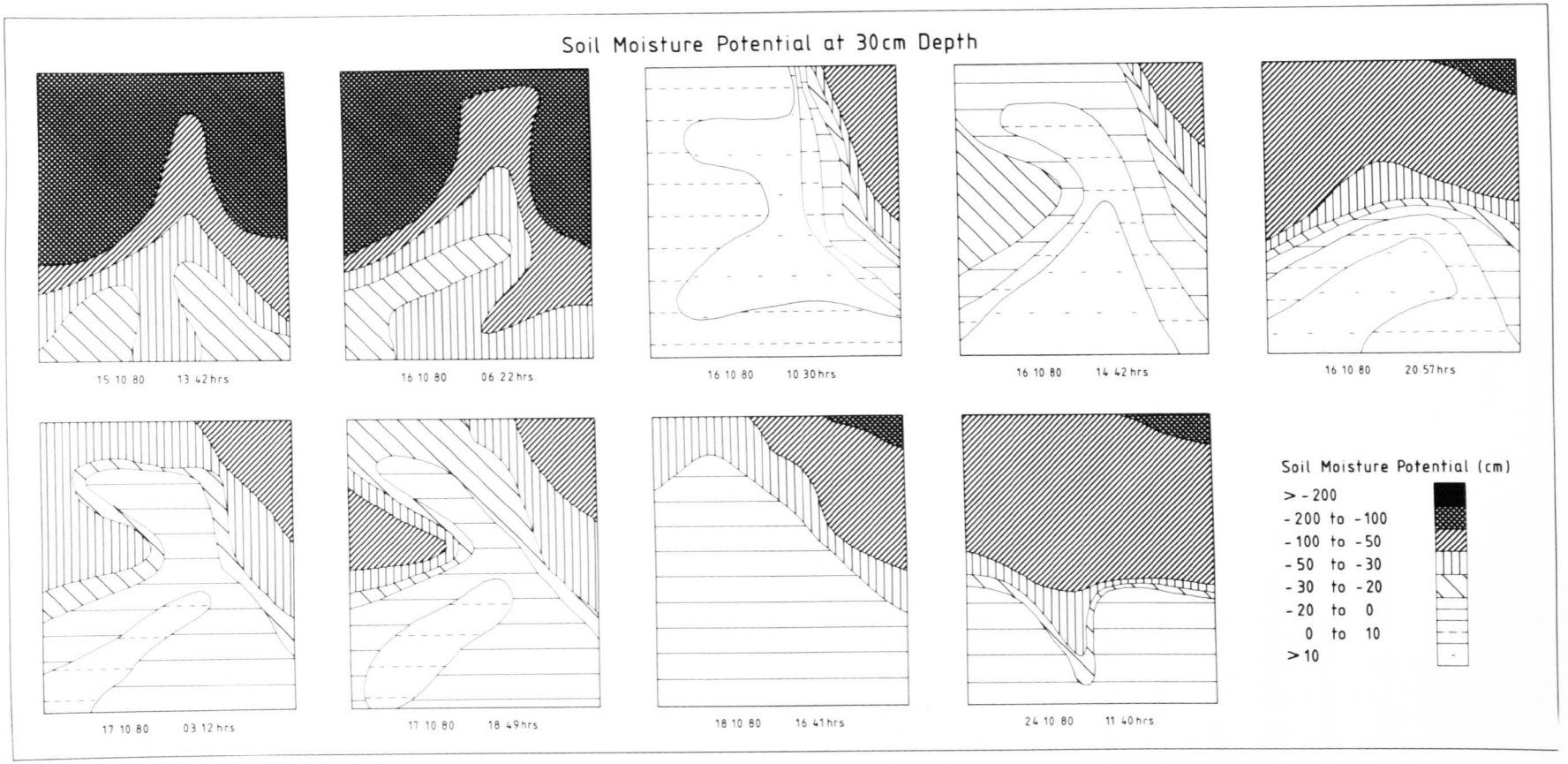

Soil Moisture Potential at 15cm Depth
15 10 80 13 42 hrs
16 10 80 06 22 hrs
16 10 80 10 30 hrs
16 10 80 14 42 hrs
16 10 80 20 57 hrs
17 10 80 03 12 hrs
17 10 80 18 49 hrs
18 10 80 16 41 hrs
24 10 80 11 40 hrs
Soil Moisture Potential (cm)
> -200
-200 to -100
-100 to -50
-50 to -30
-30 to -20
-20 to 0
0 to 10
>10

Figure 4.10


Soil Moisture Potential at 30cm Depth
15 10 80 13 42 hrs
16 10 80 06 22 hrs
16 10 80 10 30 hrs
16 10 80 14 42 hrs
16 10 80 20 57 hrs
17 10 80 03 12 hrs
17 10 80 18 49 hrs
18 10 80 16 41 hrs
24 10 80 11 40 hrs
Soil Moisture Potential (cm)
> -200
-200 to -100
-100 to -50
-50 to -30
-30 to -20
-20 to 0
0 to 10
> 10

progresses the upslope section of the slope drains and soil water converges in a saturated zone in the lower slope. By 24 10 80 the saturated area diminishes with a corresponding increase in tensions upslope which were attributable to drainage, as potential evapotranspiration, at this time of year, was too low being less than 1mm day^{-1}. The importance of topography and the development of saturated zones in hillslope hollows has been described by Anderson and Burt (1978b) and Anderson and Kneale (1980) but the development of the saturated wedge in this case was attributable to the subsurface clay horizon as well as the presence of a minor hollow on the hillslope. This sequence of events was not a regular occurrence and was only observed when there was a rainstorm with a minimum value of approximately 20mm. During the remaining winter and spring months the saturated zone was maintained at the base of the slope with only slight extension for each small rainfall event. During the growing season, precipitation temporarily decreased the S.M.D. in the surface horizon and only rarely did water move laterally or vertically through the profile. Tensiometer data shows that only the top 15cm of soil and litter was affected by incoming rainfall and this was probably taken up and transpired by plants. Soil moisture potentials at greater depths remained fairly constant as illustrated by the small soil moisture deficit.

Samples of soil water from the throughflow pits were only obtained in significant volumes (greater than 250ml for each 1m length of gutter) when saturated conditions prevailed upslope, as on 16 10 80. In fact, throughflow was only intercepted at any depth on twelve occasions throughout the 19 month period. The free face of the throughflow pit was at atmospheric pressure and throughflow can only be collected when saturated conditions exist, whereby water is able to leave the free face.

In unsaturated conditions a saturated wedge must build up behind the pit wall and the majority of rainfall events were of insufficient volume to create such a wedge. The absence of regular throughflow events indicated that the saturated zone at the base of the slope was maintained by an alternative means. Augering showed that the clay layer at the slope base was found at progressively greater depths upslope and was not encountered within 1.5m of the soil surface in either of the throughflow pits. Consequently soil water drained freely until the clay layer was encountered and then flowed laterally to augment the saturated area with tensiometers and pits at insufficient depths to monitor the flux. A greater understanding of the hillslope hydrology necessitated investigation of water-table levels and further dye tracing experiments.

4.3.0. Groundwater Hydrology

A major feature of the hillslope site was the development of a perched water-table during the months from late September to April of both years. The rapid percolation of water through the soil to the underlying, relatively impermeable, clay drift led to an accumulation of water thus creating the perched water-table. In summer months no evidence of the perched water-table was found. In winter, soil water moved through the soil profile until it reached the water-table level and a three dimensional response in groundwater movement was initiated. Rock type and soil characteristics play an important role in determining the rate and extent of groundwater fluxes. The sandstone and shales underlying the upper section of the drainage basin were porous and relatively permeable which permitted the free movement of groundwater, whilst the soil had a high value of saturated hydraulic conductivity.

Groundwater levels were monitored at boreholes 1 and 2 from October 1980 and when the potential importance of the perched water-table was realised additional boreholes were installed. Figure 4.11 illustrates the plotted weekly water-table levels in boreholes 1 to 4. The first detected levels in boreholes 1 and 2 in October 1980 coincided with the heavy rainfall and throughflow occurrences described in section 4.2.2. This period represented a return to field capacity and the development of the perched water-table ensued. By July 1981 the water-table at boreholes 1 and 2 had fallen below three metres and was not detected again during the study period. The plots for boreholes 1, 3 and 4 show the decrease in the water-table depth downslope. However, the water-table at borehole 2 is always the lowest despite being at the base of the slope. This evidence, together with textural analysis of excavated soil showed that the clay drift was not present in the area between the footpath and the drainage channel. The levels of water at boreholes 2, 5 and 6 probably represent the true water-table. All plots in Figure 4.11 show a sharp fall in water-table level when rainfall inputs are small. Linear regression analysis of weekly rainfall volumes and the depth of the water-table from the soil surface at borehole 1, for 35 samples, showed an inverse regression coefficient of -0.4096 which was significant at the 98% level. Perched groundwater levels responded to rainfall events in early September of both years well before field capacity was attained in any soil horizon. This observation supported the possibility that macropore flow was the main mechanism of soil water movement and recharged the groundwater before the soil profile reached saturation.

From mid-July, evapotranspiration and the subsequent S.M.D. prevented the replenishment of the water-table and no water levels were recorded. At the end of September 1981 the perched water-table was only detected in

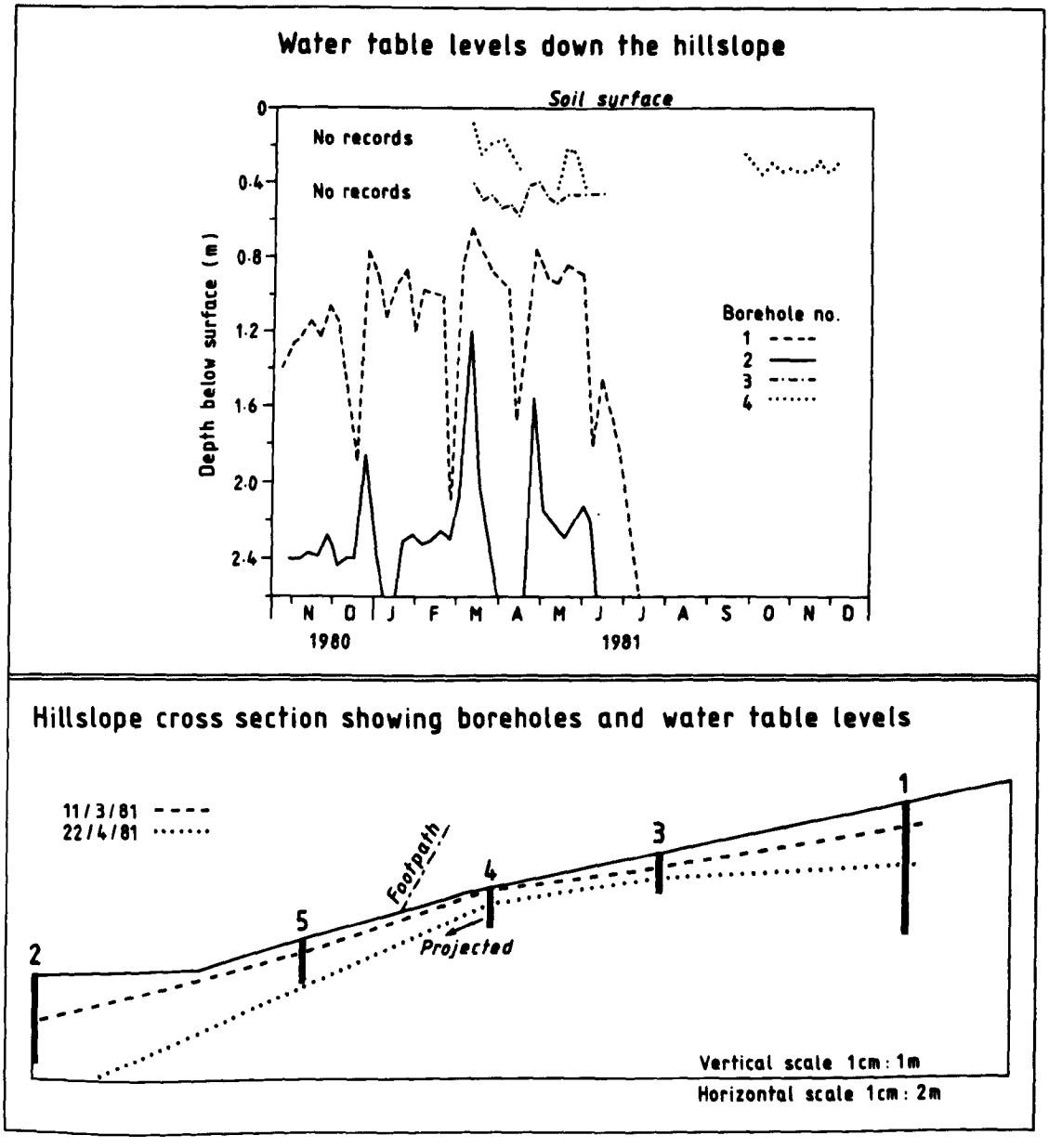

Water table levels down the hillslope
Soil surface
No records
No records
Depth below surface (m)
0
0·4
0·8
1·2
1·6
2·0
2·4
Borehole no.
1
2
3
4
N D J F M A M J J A S O N D
1980
1981
Hillslope cross section showing boreholes and water table levels
11/3/81
22/4/81
Footpath
Projected
1
2
3
4
5
Vertical scale 1cm: 1m
Horizontal scale 1cm: 2m

Figure 4.11

borehole 4 at a depth of 0.3m. The comparatively low rainfall of November (23.0mm) and December (12.0mm) 1981 delayed the extensive redevelopment of the saturated zone at the base of the hillslope.

The positive soil mositure potentials recorded at the base of the hillslope indicated pressurised subsurface flow in a direction approximately parallel to the drainage channel and towards the main stream. Greater volumes of subsurface discharge were indicated by increased positive pressures which coincided with the lateral extension of the saturated zone and rising water-table levels. Fluorescent dye tracing with Lissamine FF confirmed this direction of flow with dye being detected at boreholes 4, 7 and 8 a few weeks after application. Saturated hydraulic conductivity was estimated to be 0.933mm min^{-1} or 1.43m day^{-1} for this period during Ocober 1981. This figure is comparable to the infiltration rates of 1.13, 2.0, 0.98mm min^{-1}. The soil in the saturated area showed strong gleyic features in the top 40cm indicating that this was a zone where the water-table lay near the soil surface for extended periods of time. Figure 4.11 shows the position of the water-table downslope on 11 3 81 and 22 4 81.

The formation of a saturated wedge at the base of the hillslope and the subsequent contribution to stream discharge supports the concept of the variable source area suggested by Hewlett and Hibbert (1967). More recent studies by Anderson and Burt (1978b), Dunne and Black (1978), Burt et al (1981) and Anderson and Kneale (1982) illustrate the importance of saturated zones in the production of subsurface run-off. Anderson and Burt (1978b) state that a prediction of outflow discharge at a slope base can be calculated using Darcy's Law (1856).

Equation 4.4

$$Q = K I A$$

where Q = hillslope discharge ($l\ s^{-1}$)

K = hydraulic conductivity ($cm\ s^{-1}$)

I = water-table slope (from tensiometer data)

A = saturated area (m^{-2})

Darcy's Law requires knowledge of the cross-sectional area of the saturated zone within the hillslope from which flow occurs. The clay drift provided a semi-impermeable boundary to the saturated area and thus allowed calculation of the area of the saturated zone. Using data from the storm event of the 16th-17th October 1980 using the following values in equation 4.5

Equation 4.5

$$K = 1.555^{-05}\ m\ sec^{-1}$$

$$I = 0.22$$

$$A = 72m^{-2}$$

The calculated hillslope discharge of 0.25 $l\ sec^{-1}$ only represents an estimate of run-off as no allowance was made for variation in saturated hydraulic conductivity and the calculation of the saturated area cannot be precise. The value does, however, indicate the relative discharge of the hillslope during a storm event in winter. If a similar discharge per unit area were applied to the entire catchment a total subsurface run-off 239.0 $l\ sec^{-1}$ would result for this storm event. This figure assumes an equal

run-off for hillslope hollows and spurs which in reality would not exist. The volume of hillslope discharge adequately accounts for total stream discharge thus inferring that subsurface flow in the basin is capable of providing storm hydrographs.

4.4.0. Surface Drainage

Several ephemeral streams supply channelled flow to the main stream in the basin and thus contribute to total surface drainage and the subsequent output. Channelled flow formed the final stage in the basin hydrological cycle and stream discharge was dependent on the previously described hydrological processes.

The presence of water flowing in the ephemeral drainage channel was originally attributed to the convergence of lateral flow in the A horizon and litter, but channel side troughs did not collect sufficient water to account for the flow. The presence of flow did, however, coincide with the rising water-table monitored at borehole 1. It has been shown that subsurface water draining from the upper slope was diverted across a perched water-table before it reached the drainage channel. Flow in the channel was probably maintained by drainage from the lower slope and overspill from the perched water-table, the rising of the groundwater-table level and drainage from the opposite valley side slope. The water levels in borehole 2 probably represented the groundwater level. No quantitative measurement of flow in the ephemeral channel was made, but water samples were obtained on 30 occasions. Channel flow ceased on 20 8 80 and did not reoccur until 29 10 80 when it continued until 3 6 81. The below average rainfall in the last months of 1981 prevented the reoccurrence of channel flow, although one sample was taken on 21 10 81.

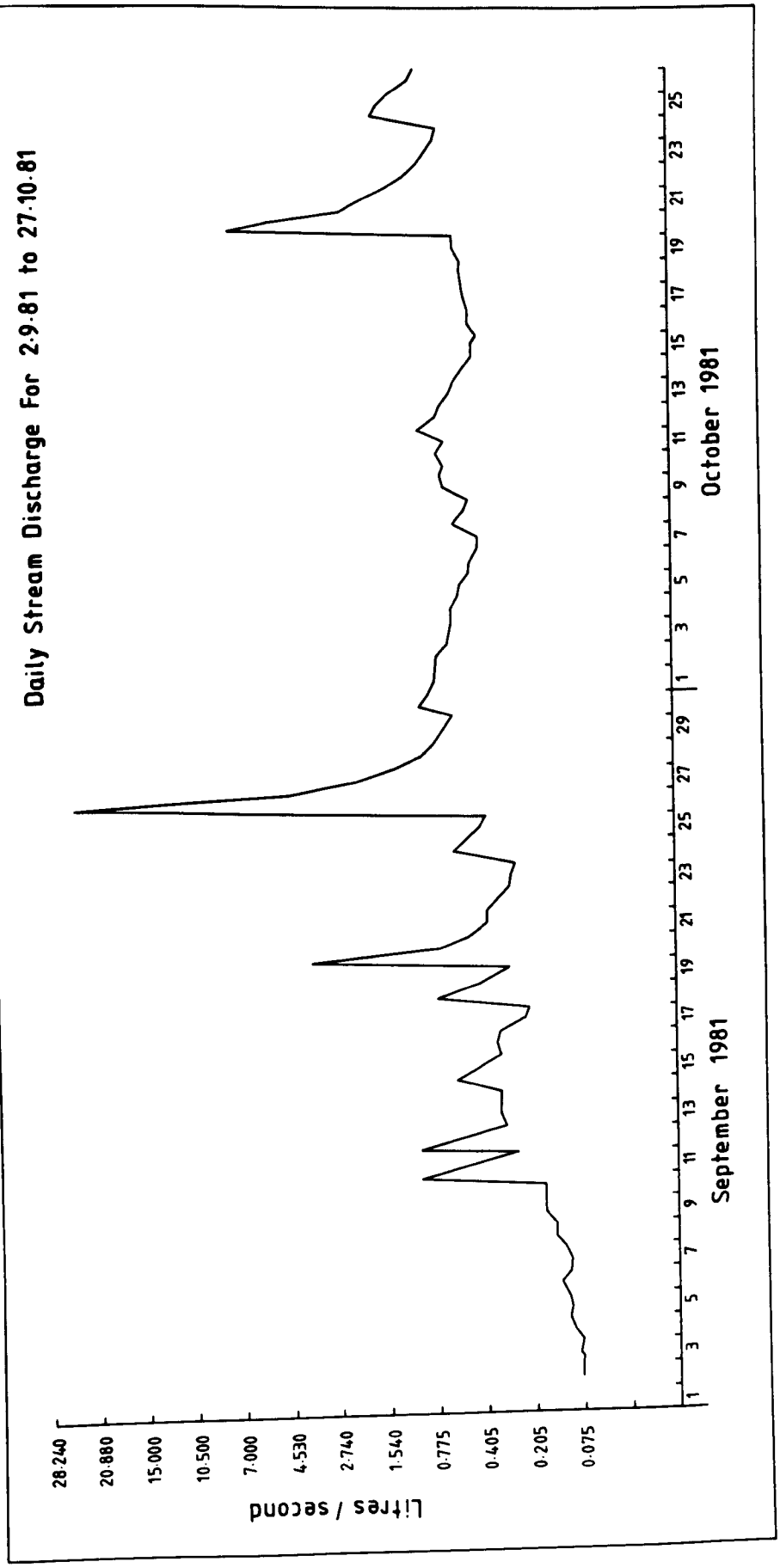

Daily Stream Discharge For 2.9.81 to 27.10.81
Litres / second
28.240
20.880
15.000
10.500
7.000
4.530
2.740
1.540
0.775
0.405
0.205
0.075
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 1 3 5 7 9 11 13 15 17 19 21 23 25
September 1981
October 1981

Figure 4.12

The mean weekly streamflow associated with each biomass sampling period is illustrated in Figure 5.7, the lowest flows being attributed to the summer and autumn months, with peak flow occurring in March 1981. The minimum discharge recorded was 0.25 l sec^{-1} on 26 9 80 and the maximum, 88.27 l sec^{-1}, was recorded on 20 12 80. The high variance of 189.1% illustrates that a wide range of flow conditions occurred during the study period. Figure 4.12 plots the daily stream discharge from 2 9 81 to 27 10 81 and this period incorporated the two main flow conditions observed in this drainage basin, that is, a low flow rate in September and increased discharge resulting from the wetting up of the soil in late autumn. Only 6mm of rain fell in the three week period prior to September and the total evapotranspiration total for August was 82.9mm. The low discharge represents minimum flow conditons which were maintained by slow groundwater seepage. During the growing season incoming water was intercepted or taken up by plants to be returned to the atmosphere by evapotranspiration. A S.M.D. was created which had to be replenished before a significant contribution of subsurface water to streamflow could be made. For example, a storm event of 39.5mm on 6 8 81 initiated a peak discharge of 20 l sec^{-1}, whereas in winter when the S.M.D. was zero a similar amount of rainfall initiated a maximum discharge of 88.0 l sec^{-1}. The daily rainfall for September to October 1981 is shown in Figure 4.13 and stream hydrographs began to respond to the rainfall input when the S.M.D. was gradually replenished. Potential evapotranspiration during this period was decreasing with monthly totals of 55.8mm and 29.5mm for September and October respectively. The soil moisture status for this period can be seen in Figures 4.14 to 4.16 which describe the late summer and autumn soil moisture potentials at 15 and 30cm depths. Negative potentials on the entire hillslope were typical during the summer and early autumn months. When evapotranspiration

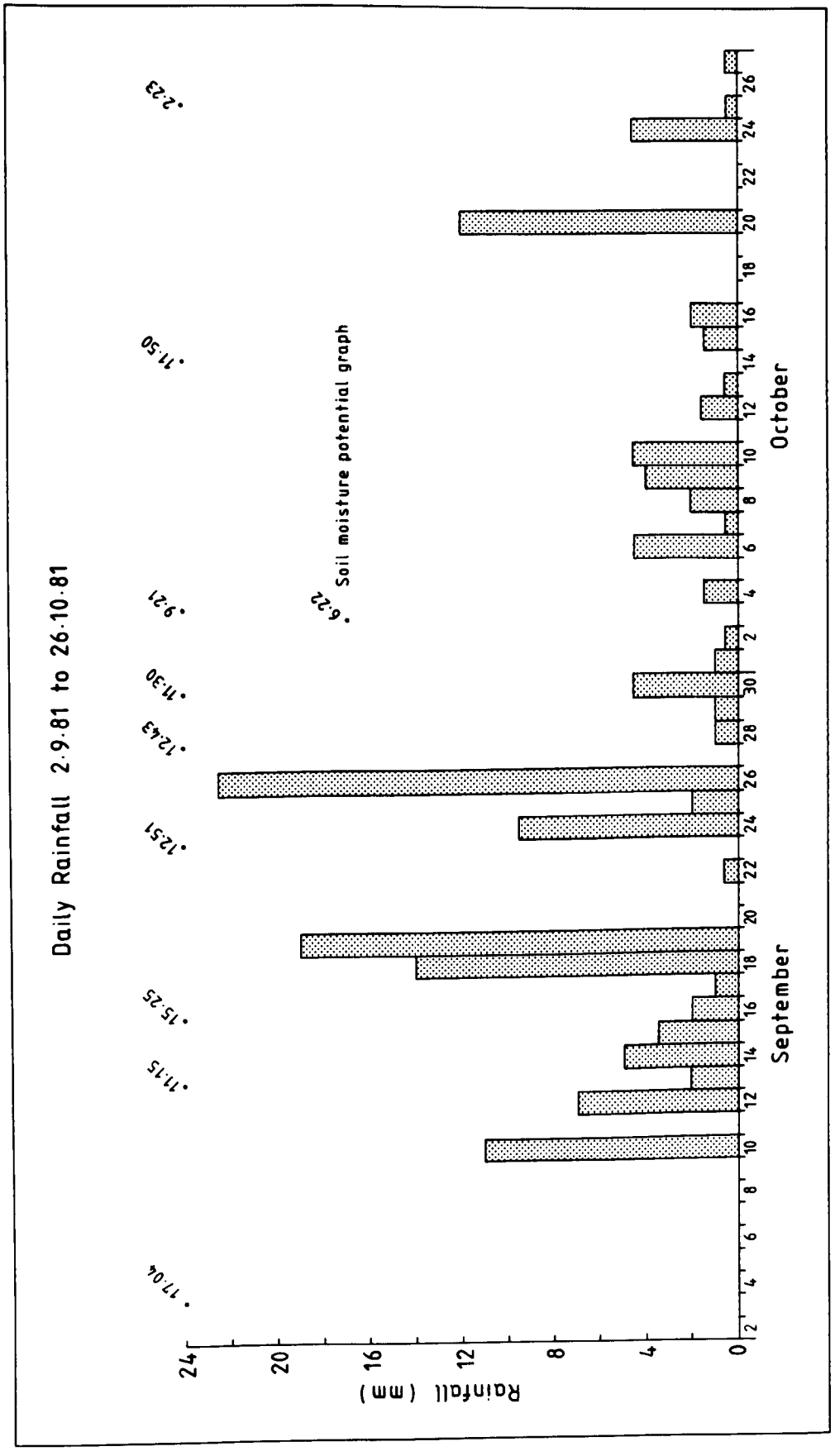

Daily Rainfall 2.9.81 to 26.10.81
Soil moisture potential graph
Rainfall (mm)
0
4
8
12
16
20
24
September
October
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
2
4
6
8
10
12
14
16
18
20
22
24
26
.17.04
.11.15
.15.25
.12.51
.12.43
.11.30
.9.21
.6.22
.11.50
.2.23

Figure 4.13

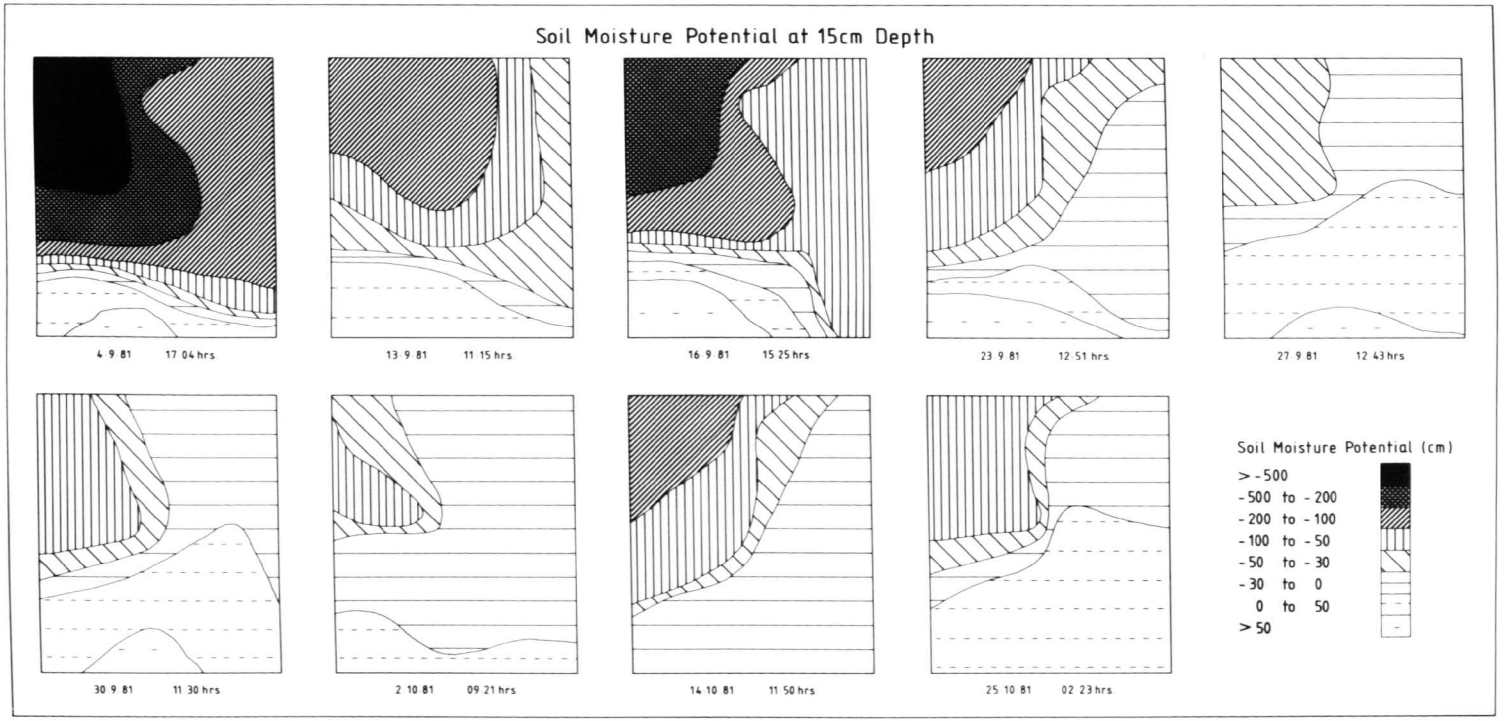

Soil Moisture Potential at 15cm Depth
4 9 81 17 04 hrs
13 9 81 11 15 hrs
16 9 81 15 25 hrs
23 9 81 12 51 hrs
27 9 81 12 43 hrs
30 9 81 11 30 hrs
2 10 81 09 21 hrs
14 10 81 11 50 hrs
25 10 81 02 23 hrs
Soil Moisture Potential (cm)
> -500
-500 to -200
-200 to -100
-100 to -50
-50 to -30
-30 to 0
0 to 50
> 50

Figure 4.14

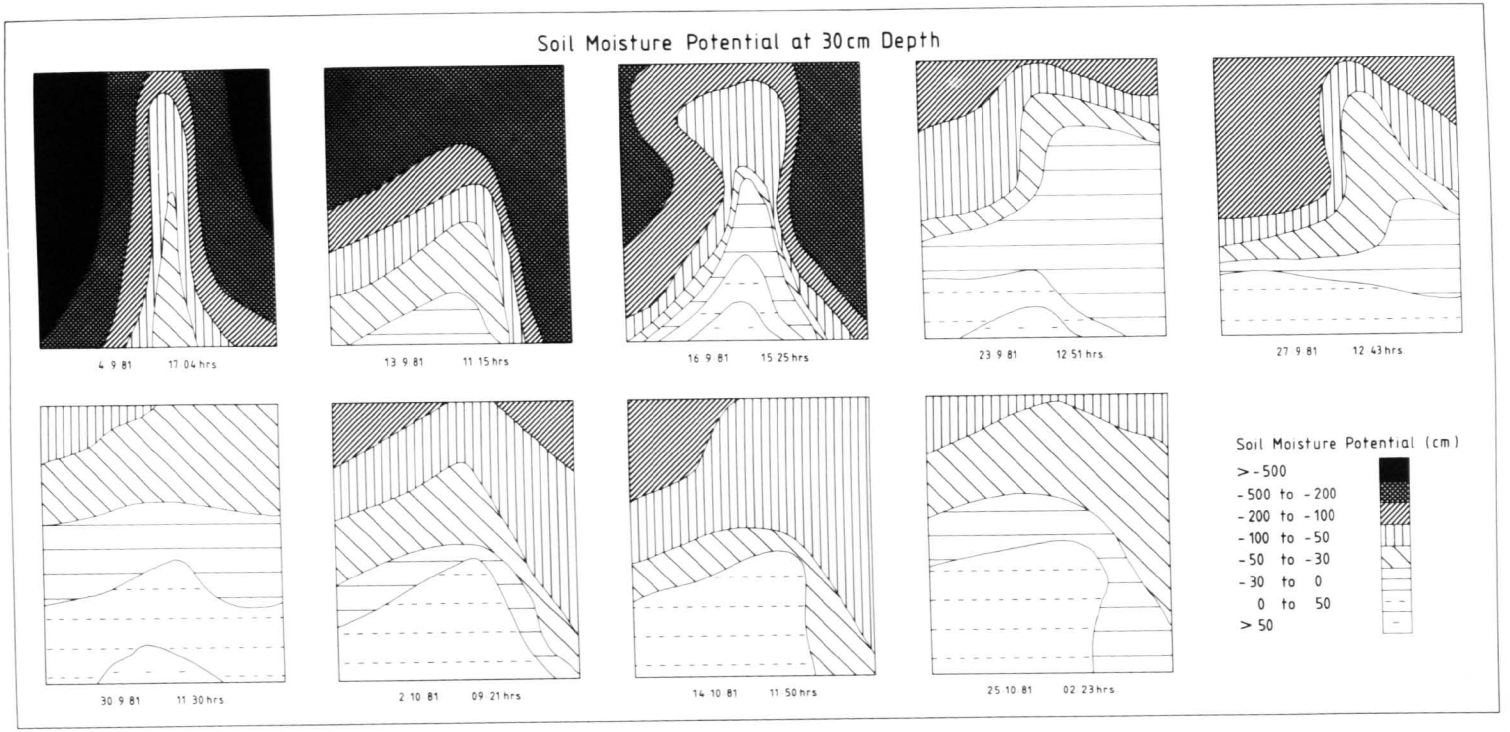

Soil Moisture Potential at 30cm Depth
4 9 81 17 04 hrs
13 9 81 11 15 hrs
16 9 81 15 25 hrs
23 9 81 12 51 hrs
27 9 81 12 43 hrs
30 9 81 11 30 hrs
2 10 81 09 21 hrs
14 10 81 11 50 hrs
25 10 81 02 23 hrs
Soil Moisture Potential (cm)
> -500
-500 to -200
-200 to -100
-100 to -50
-50 to -30
-30 to 0
0 to 50
> 50

Figure 4.15

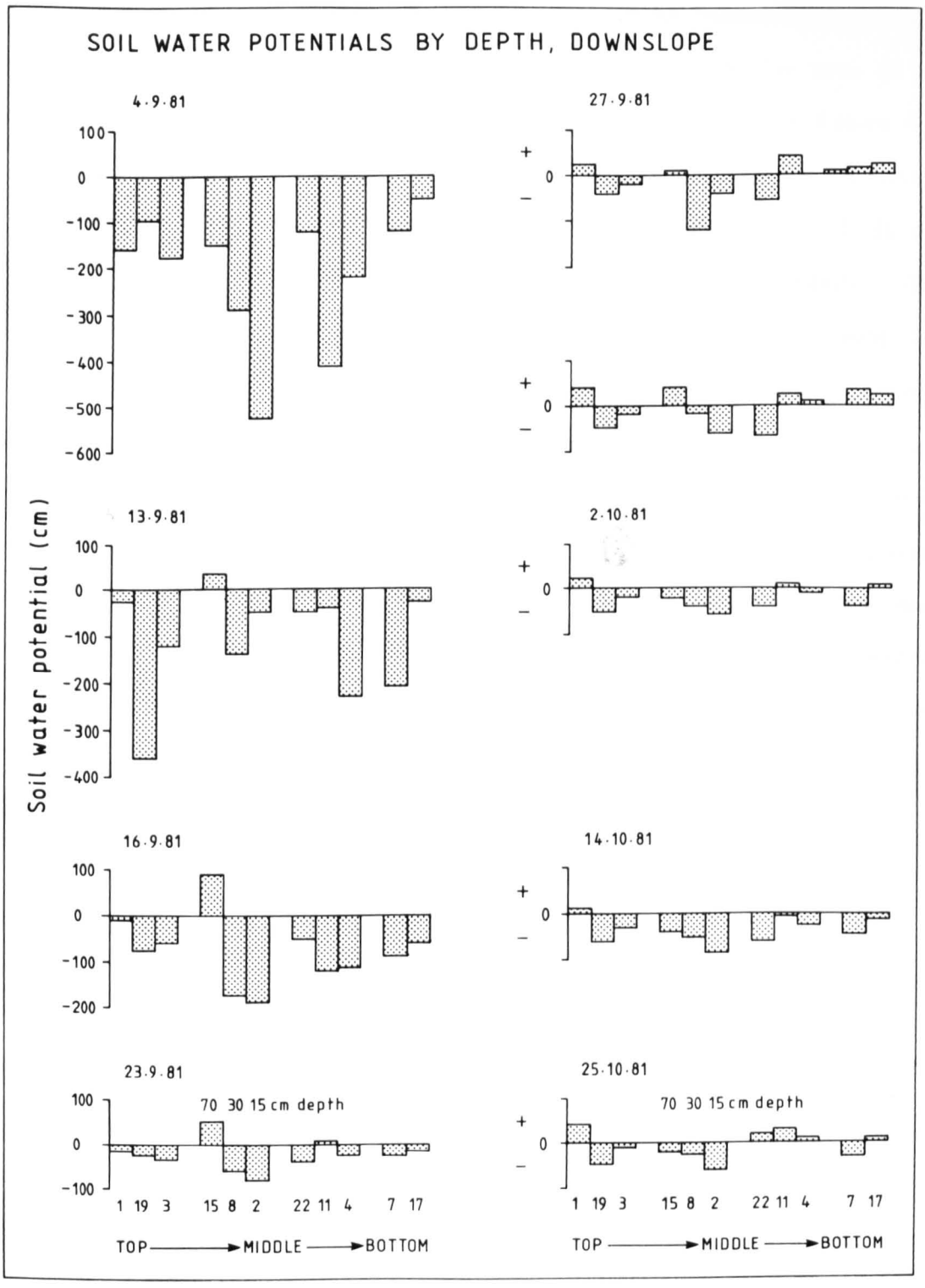

SOIL WATER POTENTIALS BY DEPTH, DOWNSLOPE
4·9·81
27·9·81
13·9·81
2·10·81
16·9·81
14·10·81
23·9·81
25·10·81
Soil water potential (cm)
100
0
-100
-200
-300
-400
-500
-600
+
0
−
70 30 15 cm depth
1 19 3 15 8 2 22 11 4 7 17
TOP → MIDDLE → BOTTOM

Figure 4.16

decreased in late September the S.M.D. began to be replenished and by 25 10 81 moisture potentials were positive, particularly at the base of the slope, indicating saturated conditions. Storm hydrographs in Figure 4.12 show sharp rises followed by a gradual exponential decrease in discharge, for example, a storm event commenced at 24.00 hours on 24 9 81 and ceased at 08.30 hours on 26 9 81 contributing 22mm of rainfall. The stream hydrograph began to rise after only 30 minutes from the commencement of rainfall. Peak discharge was reached when the rainfall ceased, exhibiting a 4 hour time lag between peak rainfall intensity and maximum discharge, whereby the hydrograph declined gradually and after a three day rain free period reached a constant level with discharge greater than the pre-storm flow. This course of events illustrates the rapid response of stream discharge to rainfall during the autumn/winter months. Infiltrating water moved quickly to the perched water-table via macropores and then travelled as saturated flow towards the stream. The fairly high lateral, saturated hydraulic conductivity (0.933mm min^{-1}) of the soil ensured rapid flow and the soil water entering the stream consisted of displaced water from saturated zones adjacent to the channel.

During the summer months the baseflow component of the stream hydrograph (Gregory and Walling, 1973) was derived from the groundwater in the underlying sandstones and shales. Summer rainfall events, though large, only cause a minor rise in the hydrograph and for the majority of the summer time stream flow was fairly constant and unresponsive to small rainfall inputs.

Total stream run-off was expressed in terms of the loss of the equivalent depth of water from the upper section of the drainage basin. A fairly accurate calculation could be made as continuous records of discharge were obtained by the stage recorder. The total loss of water for the entire study period was 321.6mm.

Table 4.8 gives the monthly water balance for the water year October 1980 to September 1981. Total precipitation input was 672mm and run-off was 250mm. Similar storage conditions exist at the beginning and end of the water year (Gregory and Walling, 1973) and therefore rainfall minus run-off can be attributed to evapotranspiration, though an unknown amount may be attributable to deep seepage from the basin. The calculated evapotranspiration only exceeds the rainfall in one month, suggesting that a S.M.D. does not develop in the soil. Actual S.M.D. data shows that the maximum deficit which does occur is 38.2mm which was very low (Hodgson, 1974).

4.5.0. **Conclusion**

The flow diagram shown in Figure 4.17 summarises the hydrological pathways which were identified in the drainage basin. The volumes in mm of water refer to the total study period. The overall relationship between water storage and fluxes in the drainage basin was calculated according to the water balance equation (Gregory and Walling, 1973).

Equation 4.6

$$P = Q + E \pm S$$

where

P = total precipitation

Q = total streamflow

E = total evaporation loss

S = change in storage

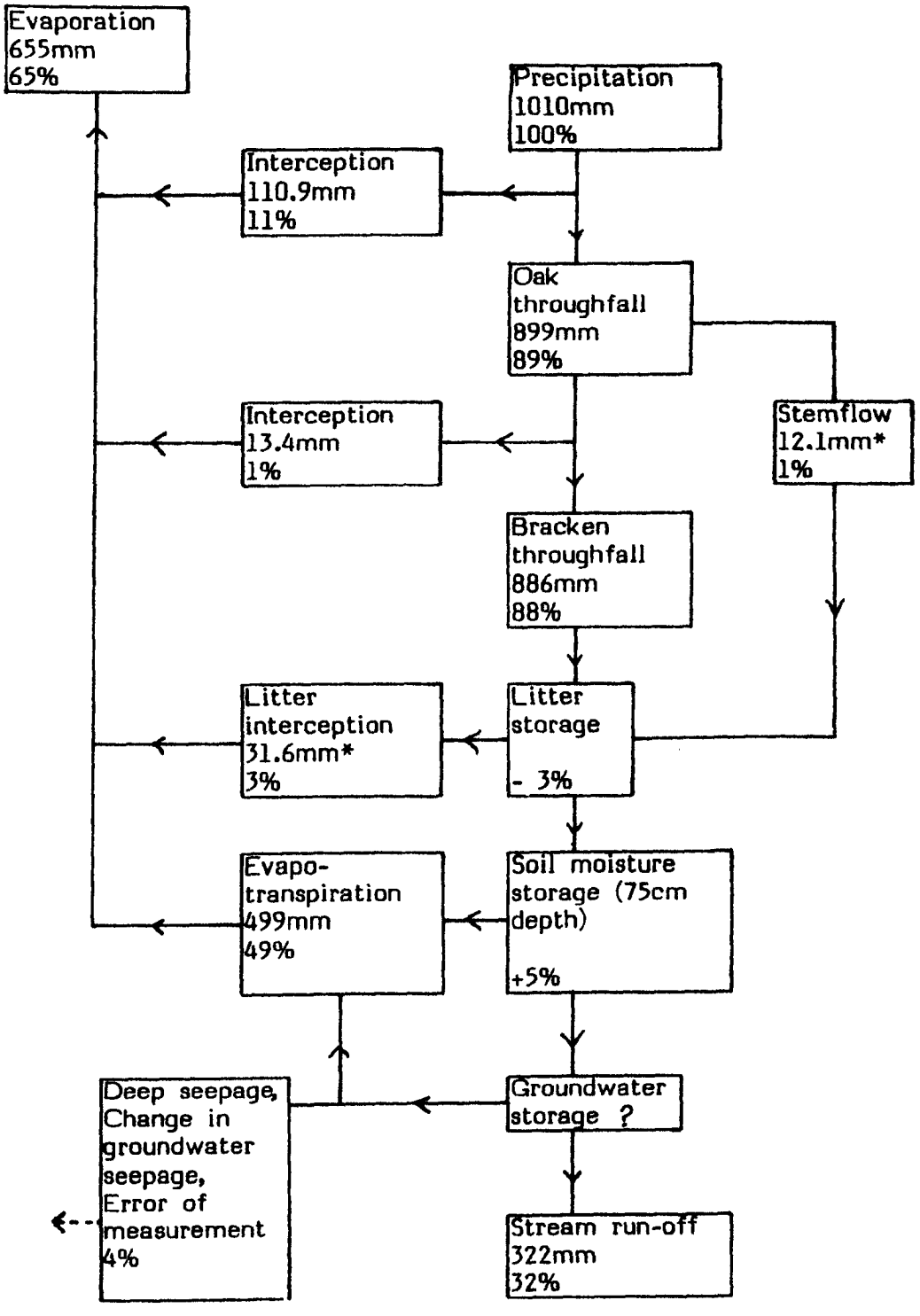
Table 4.8 **Monthly water balance 1980-81**

	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Total
Monthly rainfall(mm)	68.0	45.0	49.0	28.0	43.0	88.0	43.0	71.0	27.0	32.0	63.0	115.0	672.0
Monthly run-off(mm)	8.1	18.9	40.1	21.9	43.5	44.7	30.3	31.0	4.7	2.3	1.6	3.0	250.1
Rainfall - run-off(mm) evapotranspiration	59.9	26.1	8.9	6.1	-0.5	43.3	12.7	40.0	22.3	29.7	61.4	112.0	421.9
Monthly S.M.D	0.0	0.0	7.0	14.0	0.0	15.0	7.0	14.0	32.0	33.0	30.0	10.0	
Actual Evapotranspiration	59.9	26.1	15.9	20.1	-0.5	58.3	19.7	54.0	54.3	62.7	91.4	122.0	

water year = 1st October 1980 to 30th September 1981

Figure 4.17 **Summary of hydrological pathways**

Values are totals June 1980 - December 1981



* estimated values

Nearly 50% of the initial precipitation input was returned to the atmosphere by evapotranspiration whilst vegetation and litter interception accounted for a further 15% of evaporation losses. Stream run-off repesented 32% of the total rainfall input for the study period. The remaining 4% may be attributable to inaccuracy of measurement or possibly deep seepage. The sandstones and shales underlying the basin are permeable and water may have been lost by transfer to adjacent basins or deep seepage.

Chapter 5.0 WATER, SOIL AND VEGETATION CHEMISTRY

5.0.0. Introduction

Nutrients within a forested ecosystem are in a continuous state of change, with concentrations at each level of the system depending on the many biogeochemical proceses which operate within the basin. The best known catchment study is that of the Hubbard Brook Experimental Forest, New Hampshire, U.S.A. and Likens et al (1977) summarise the main findings of the project, which investigated the input and output of chemical elements for several drainage basins and examined many of the catchment processes. However, the pedological processes and soil chemistry have not been considered in detail. Other works have not considered nutrient-hydrologic interactions in such detail and concentrate on the calculation of input or input/output nutrient budgets. For example, Carlisle et al (1966a, 1966b) and Cryer (1976) consider precipitation inputs, whilst many authors have investigated river or stream water quality, for example Douglas (1972), Walling and Foster (1975), Ternan and Williams (1978) and Reid et al (1981). The in situ process of nutrient cycling and the growth of individual species of plants such as bracken and oak is well documented. Watt (1976) has published a series of papers on the ecology of bracken and other investigations include those of Ferguson and Armitage (1944), Hunter (1944), Frankland (1966, 1976), Callaghan et al (1981) and Chen and Lindsey (1981). The importance of nutrient inputs via stemflow and litter from oak have been largely investigated by Carlisle et al (1966a, 1966b) and Bocock (1963), but their work has not studied the extent to which soil and water chemistry are influenced by these inputs. Nutrient fluxes and stores are closely related to hydrological pathways and it is therefore impossible to consider water, soil and vegetation chemistry in isolation. This chapter therefore describes the fluxes of nutrients from the

atmosphere, within the soil matrix and the loss of nutrients in stream water. The role of vegetation is considered in terms of nutrient uptake and release.

5.1.0. Precipitation Chemistry

The atmosphere provides nutrients not only in precipitation but also in dry fallout and Eriksson (1960) believes that the latter input may be two to four times more important than that of wet precipitation. The interpretation of precipitation chemistry data requires an understanding of the origin of elements in the atmosphere. Bouwer (1978) quotes volcanic eruptions, dust, sea water, gaseous metabolic products, lightning and cosmic ray reactions, industry and agriculture to be amongst the most important sources. Many studies have been undertaken to investigate the composition of rainfall with particular reference to sulphur and acidity (for example, Likens and Bormann, 1974; Martin, 1979; Likens et al, 1979. Studies on the general composition of rainfall have been made by Gorham (1958), Bormann and Likens (1967), Allen et al (1968), Fisher et al (1968), Cryer (1976) and Reid et al (1981).

Artificial and natural contaminants are removed from the atmosphere by wet and dry precipitation and both types are measured as bulk precipitation in this study. When raindrops leave a cloud base they pick up large aerosol particles and as the raindrops fall to the ground they lose moisture by evaporation, thus increasing solute concentration and acidity (Junge, 1963). Little is known, however, of the efficiency and variation of such processes. Cryer (1976) reports a large variation in solute concentration for each rainfall event due to washout, evaporation, meteorological conditions and antecedent events, causing the investigation of solute origins to be complex. The same author was unable to relate rainfall chemistry to the prevailing weather conditions.

A variety of statistical techniques have been employed in the past to determine the origin of solutes in precipitation. For example, Reid et al (1981) used factor analysis to group similarly derived solutes, whilst Cryer (1976) employed synoptic indices and multiple regression analysis to explain precipitation chemistry. Most workers, however, have compared solute ratios in precipitation with those in sea water. Similar ratios denote oceanic origins and changes in the ratio indicate an alternative source, for example Gorham (1958) and Junge (1963). The ratio assumption has been criticised by Koyama and Sugawara (1953) who stated that during volatilisation at the ocean surface, separation of elements may occur and atmospheric ratios above the ocean may be different from those in seawater. There is little doubt, however, that some elements do derive from ocean spray and Reid et al (1981) found that sea spray had a dominant influence on the composition of precipitation in north-east Scotland.

Figure 5.1 presents the plotted rainfall chemistry for each solute monitored in association with pH, the negative logarithm of the hydrogen ion activity and specific conductance. All values represent the mean weekly input of nutrients (kg ha^{-1}) for each biomass sampling period with the exception of specific conductance and pH which are not volume weighted. A summary of gross precipitation characteristics is provided in Table 5.1. The origin and explanation of solute levels in rainfall was initially determined by a cross correlation matrix which identified significant linear relationships between solute levels, acidity and precipitation volume (Table 5.2).

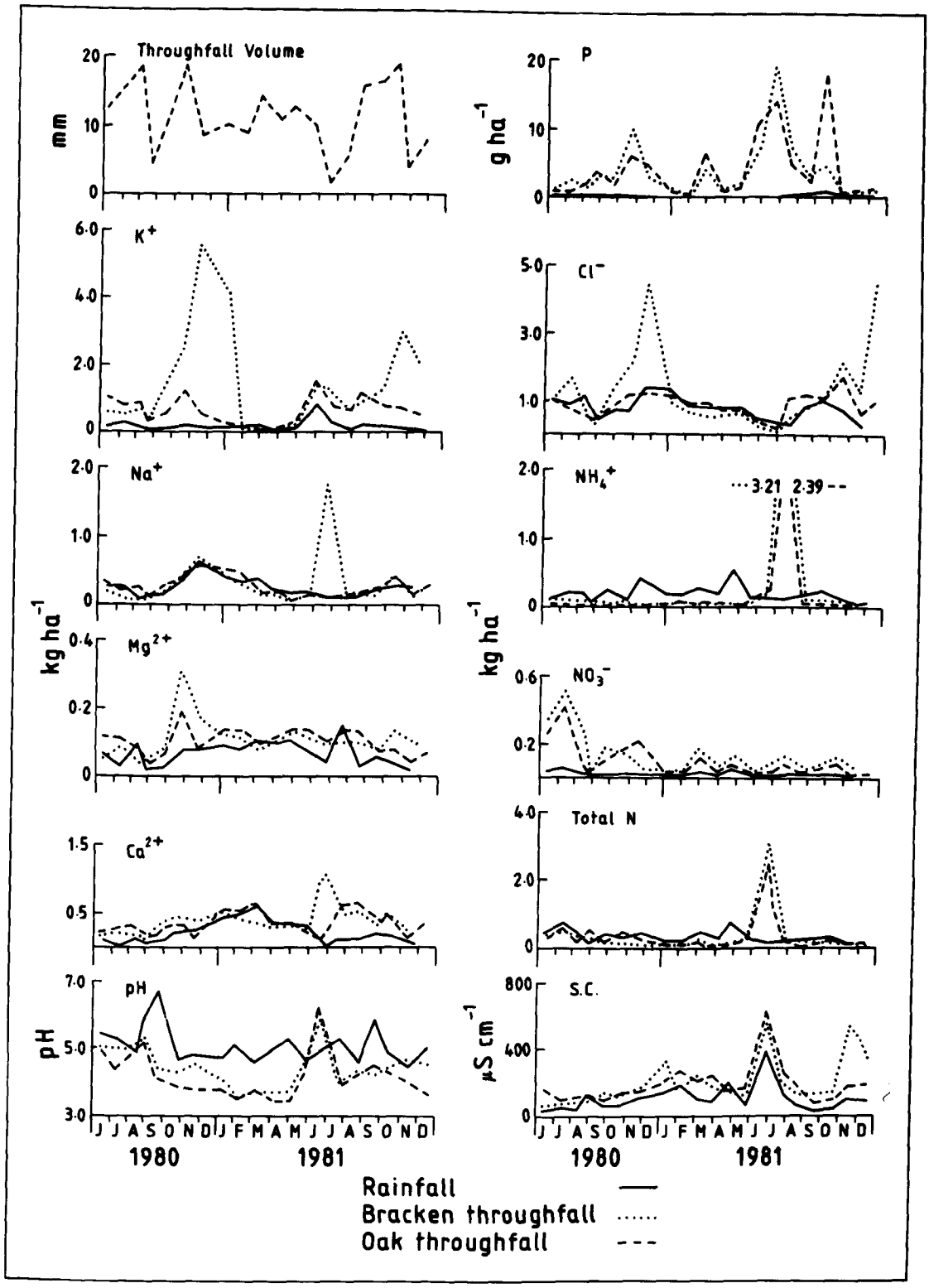


Figure 5.1 Precipitation Chemistry

Table 5.1 **Rainfall and throughfall characteristics**

		Ca	Mg	Na	K	NH_4	NO_3	NO_2	Cl	P	Sc*	pH*
$\bar{x}$ kg ha^{-1} wk^{-1}	M	0.28	0.006	0.26	0.14	0.19	0.16	0.01	0.78	0.003	104.7	4.58
	O	0.41	0.11	0.28	0.97	0.18	0.12	0.01	0.88	0.04	172.4	3.63
	B	0.41	0.12	0.32	1.26	0.16	0.11	0.01	1.23	0.04	177.1	3.82
% variance	M	96.4	100.0	107.7	150.0	126.3	118.8	300.0	93.6	800.0	125.0	35.1
	O	102.4	90.9	107.1	119.6	666.7	158.3	633.3	93.2	225.0	82.0	44.8
	B	126.8	91.7	250.3	164.3	595.7	163.6	300.0	148.8	200.0	98.0	40.5
SE	M	0.03	0.01	0.03	0.02	0.03	0.02	0.0	0.08	0.01	14.99	0.183
	O	0.05	0.01	0.03	0.13	0.11	0.02	0.02	0.09	0.01	16.22	0.186
	B	0.06	0.01	0.09	0.24	0.16	0.02	0.0	0.21	0.01	19.99	0.177
Maximum kg ha^{-1} wk^{-1}	M	1.31	0.29	1.92	1.41	1.52	1.00	0.27	3.62	0.26	1058.0	8.60
	O	2.62	0.43	1.72	5.30	8.70	0.86	1.35	3.28	0.58	918.0	6.90
	B	3.66	0.48	6.76	14.03	11.96	0.87	0.21	11.76	0.55	1015.8	6.85

Sample size = 76

* unweighted variables

Table 5.2 **Correlation matrix for solute concentrations in rainfall**

	Ca	Mg	Na	K	NO_3	Cl	pH	SC	NH_4	NO_2	P	Volume
Ca												
Mg												
Na		+										
K		+	+									
NO_3		+	+									
Cl		+	+		+							
pH		+	+	+	+	+						
SC		+	+	+	+	+	+					
NH_4												
NO_2	+											
P												
Volume		-					-		+	+		

Sample size = 63

\+ significant positive correlation

\- significant negative correlation

confidence level = 95%

It is generally agreed that the majority of sodium, chloride and magnesium in the atmosphere is derived from the ocean. Isoline plots of chloride concentration in rainfall show decreases in concentration inland, (Gorham, 1958; Junge, 1963; Stevenson, 1968). The chloride to sodium ratio in seawater is 1.8 and calculation of the mean weekly rainfall ratio for this area gave a value of 3.0, indicating an alternative source of chloride. Junge (1963) states that chloride produced by industry raises the ratio in

England to 3.0 - 4.0, whilst Gorham (1958) found significant correlations between chloride and acidity suggesting origins from the combustion of coal. Table 5.2 shows significant intercorrelations between sodium, chloride and magnesium suggesting similar origins or mechanics of fallout. Chloride, however, shows a positive correlation with pH, in contrast to Gorham's findings. The proximity of a large industrial conurbation and a coal fired power station probably contribute to chloride surpluses. Chloride also correlates positively with nitrate, which is another major industrial pollutant again suggesting similar origins. Figure 5.1 shows that both sodium and chloride exhibit winter peaks corresponding to the seasonal increase in the use of fossil fuels and oceanically derived concentrations in frontal rainfall.

The sodium to potassium ratio in seawater is 28.0. The ratio is probably high because potassium is derived mainly from terrestrial sources and exhibits extremely low oceanic concentrations. The mean weekly ratio for precipitation in this area is 1.86, indicating an enrichment of rainwater by potassium from an alternative source to the ocean. The exact source is unknown but Likens et al (1977) believe that soil particles in the atmosphere may react with hydrogen ions and become 'weathered', releasing solutes. Table 5.2 shows a significant positive correlation between potassium and pH, which suggests weathering release with increasing alkalinity. Galloway and Likens (1976) suggest that pollen and organo metallics released by vegetation may supply significant quantities of nutrients including potassium. Figure 5.1, however, shows that inputs to the ecosystem of potassium are very small in comparison to other elements, but Table 5.18 shows that the input is sufficient to maintain the balance of ions within the ecosystem.

Calcium does not correlate significantly with any ion except nitrite indicating a completely separate origin. Little calcium is derived from the sea (Junge, 1963) and Allen et al (1974) suggest that agricultural liming clouds can rise to considerable heights and travel great distances, whilst limestone quarrying can introduce calcium based dust in the atmosphere (Crabtree and Trudgill, 1981). In this area Pre-Cambrian diorite within the Cambrian Shales is blasted daily and X-ray fluorescence analysis of the shales shows significant amounts of calcium are present. In addition, North Warwickshire is predominantly agricultural with lime being applied between autumn or spring ploughing and the planting of crops. Figure 5.1 illustrates that calcium levels increase steadily through autumn to a spring maximum falling to negligible levels in summer. Magnesium tends to follow this pattern and part of its origin may also derive from agricultural limes. However, the winter maximum of magnesium may also be attributed to oceanic origins.

Agricultural activities may help to explain levels of total nitrogen in precipitation. Ammonium nitrate is usually applied to the growing crop in spring and Figure 5.1 shows increased nitrogen in rainfall at this time. Junge (1963) states that ammonium concentrations in rainfall exhibit a seasonal pattern and are affected by acidity. Ammonium is absorbed from the atmosphere when the pH of rainfall is above 6 or 7, but Table 5.2 shows no correlation between pH and ammonium because the mean pH of rainfall during the study period was only 4.58. Ammonium in precipitation may have been derived from the ammonium acetate waste emissions of a large synthetic material manufacturing plant situated 14km to the south-south-east of the basin. Some nitrate is probably derived from the combustion of fossil fuels but the majority originates from the release of oxides of nitrogen by microbes in the soil (Grannat, 1972).

However, Figure 5.1 shows no obvious seasonal trends in nitrate levels. The input of nitrite by rainfall was extremely low, with the mean weekly value being 0.01 kg ha^{-1} (Table 5.1), probably as a result of the fact that nitrite in the atmosphere is quickly oxidised. The levels which do occur are probably of industrial origin.

Levels of atmospheric phosphate have received little attention in the literature though values between 0.008 - 1.0 mg l^{-1} have been documented (Junge, 1963; Likens et al, 1977). Table 5.2 shows that phosphate correlates significantly with no other variable and Figure 5.1 shows that phosphate concentrations in rainfall are either extremely low or undetectable by the analytical method used. Table 5.1 shows that the mean weekly input of phosphorus was 0.01 kg ha^{-1} but weekly input varied more than any other element, the coefficient of variation being 800.0%.

The pH levels of rainwater are plotted in Figure 5.1. The mean pH value over the entire study period was 4.58 with little weekly variation having a coefficient of variation of 35.1%. Rainfall is naturally acidic due to the absorption of carbon dioxide from the atmosphere but anthropogenic substances such as sulphate and oxides of nitrogen increase the acidity of rainwater to such an extent that it may be harmful to living organisms and the ecosystem structure in general. Figure 5.1 shows a seasonal trend in rainfall acidity with low values in winter, possibly due to the increased use of fossil fuels (Martin, 1976). Table 5.2 shows that pH correlates significantly with magnesium, sodium, potassium, nitrate and chloride and also inversely with precipitation volume. Magnesium, sodium and potassium are basic cations and the positive relationship is therefore expected as these ions increase the alkalinity of rainwater. The inverse relationship between rainfall volume and acidity, shows that the rainwater

derived from low magnitude rainfall events was less acidic than that derived from high magnitude events, a finding which is not comparable to the data of Junge (1963). Nitrate and chloride also provide an unexpected positive relationship with pH and therefore the low acidity of the rainfall was probably attributable to high sulphate concentrations: valuesof up to 100 mg l^{-1} were recorded for this element. Likens et al (1979) states that precipitation chemistry is dominated by hydrogen ions on an equivalent basis and pH's below 5.6 are considered to be acid. Precipitation acidity has important consequences when considering the movement of solutes through the vegetation canopy and the susequent effect on soil conditions.

Specific conductance is an approximate measure of mineral salt concentration and reflects the general trend of ionic concentration in rainfall throughout the study period (Foster et al, 1981). A seasonal trend can be observed. Figure 5.1 shows winter maxima and also a June 1981 peak which corresponded to a very low monthly rainfall volume of 27mm.

Table 5.1 summarises rainfall characteristics for each variable. Phosphorus and nitrite exhibit the most variation in concentration on a weekly basis, whilst pH shows the least variance. The remaining ions, volume and specific conductance all show a similar weekly variance which is related to storm size, intensity and duration (Junge, 1963 and Cryer, 1976).

5.1.1. Throughfall Chemistry

The importance of throughfall chemistry to the supply and redistribution of plant nutrient and other solutes has been recognised by several workers including Carlisle et al (1966a, 1966b), Eaton et al (1973) and Ternan and Williams (1978). Calculation of nutrient inputs from throughfall allows assessment of the relative importance of the input in the functioning of the ecosystem. Leaching of the vegetation canopy by falling rain provides nutrients to plants in a readily available, soluble form via the soil and it was the magnitude, frequency, duration and timing of such nutrient inputs which were of importance in this study.

Throughfall chemistry initially depends on that of incident precipitation. Table 5.3, however, shows that only calcium inputs are intercorrelated between oak and bracken throughfall and precipitation. Chloride and phosphorus loadings in oak throughfall are positively correlated with those of incident precipitation but all other inputs are significantly altered by the vegetation canopy. A vegetation surface will intercept falling rain and salts may be deposited as evaporation occurs. Alternatively, some of these intercepted solutes may be absorbed directly by the plant or by resident microflora. As water passes through the vegetation canopy it may wash off evaporates, the secretions of microflora and insects and also deposits contributed by dry fallout. Consequently it is not always possible to equate throughfall chemistry with losses from plant tissue (Carlisle et al, 1966a). The action of acid rainfall traversing the vegetation canopy can lead to the release of ions by leaching and the amount of each ion released is dependent on the morphology of the plant and the physiological function of that element. Table 5.4 shows that negative correlations exist between the volume of throughfall and element concentration though not all relationships are significant. Eaton et al (1973) suggests that the

amount of leaching is greater per unit volume of rainfall with low intensity rain storms than during a heavy storm and is also greater in the first few hours of wetting. He attributes this phenomenon to the residence time of water on the plant surface.

Table 5.3 **Rainfall and throughfall solute correlations**

	Ca	Mg	Na	K	N	Cl	P
Oak							
t'fall	.60304	.13761	.15691	.04608	.10509	.54020	.47713
Bracken							
t'fall	.50732	.04118	.13108	.20234	.10024	.40311	.08223

Sample size = 19

Critical value of r^2 at 95% = 0.4555

Figure 5.1 compares rainfall chemistry with that of both throughfall types throughout the study period and Table 5.1 identifies the characteristics of throughfall chemistry. The growth of deciduous vegetation introduces a seasonal cycle which can also be observed in the solute concentrations of throughfall. As leaves and fronds emerge they are rich in nutrients and contribute ions as leaching takes place. This process continues throughout the growing season until senescence of the annual parts approaches. Cellular breakdown, enhanced by frost activity, mobilises nutrients when cell walls rupture (Watt, 1976) and throughfall solute concentrations

Table 5.4 **Correlation matrices for solute concentrations in oak and bracken throughfall**

Bracken throughfall

	Ca	Mg	Na	K	NO_3	Cl	pH	SC	NH_4	NO_2	P	Vol
Ca												
Mg	+											
Na	+	+										
K	+	+	+									
NO_3												
Cl		+		+								
pH		+		+	+							
SC	+	+	+	+		+	+					
NH_4	+		+	+				+				
NO_2		+					+					
P	+	+	+	+				+	+			
Vol		-					+					

Oak throughfall

	Ca	Mg	Na	K	NO_3	Cl	pH	SC	NH_4	NO_2	P	Vol
Ca												
Mg	+											
Na	+	+										
K												
NO_3				+								
Cl	+	+	+									
pH	+	+	+		+	+						
SC	+	+	+			+	+					
NH_4		+					+	+				
NO_2												
P	+	+	+				+	+	+			
Vol	-	-	-			-	+					

+ significant positive correlation

- significant negative correlation

Sample size = 76

Confidence level = 95%

increase. This effect is most noticeable for potassium and chloride. These ions are complementary osmotic regulators in cell sap and are not part of the plant fabric; they are therefore more susceptible to leaching, the effect being more profound for bracken throughfall (Figure 5.1). Potassium and chloride show no significant correlation in gross precipitation (Table 5.2) and yet in bracken throughfall show a strong association emphasising the influence of vegetation on throughfall chemistry (Table 5.4). The seasonal trend is also observed in phosphate concentrations and a May 1981 peak corresponds to the leaching of the newly emerged, nutrient rich leaves and fronds. Figure 5.1 shows that phosphate in throughfall must derive from leaching in the vegetation canopy. Calcium, magnesium and sodium only show minor peaks in concentration during the autumn months. The former two are associated with organic molecules in the plant and are less susceptible to leaching. Sodium concentrations, in both types of throughfall, follow the pattern of rainfall concentration fairly closely, illustrating the low concentration of labile sodium in the aerial parts of bracken and oak. Figure 5.1 shows that throughfall pH is usually lower than rainfall and exhibits a distinct seasonal fluctuation with summer peaks and a winter trough. During summer months basic ions are released from the vegetation canopy by hydrogen ion exchange (Eaton, 1973) thus increasing pH and Table 5.4 shows positive correlations of most ions with pH. With the onset of dormancy ion exchange is limited and hydrogen ions appear in throughfall. The water, however, is still more acidic than rainfall. Table 5.1 shows the mean oak throughfall pH to be 3.63 whilst rainfall is 4.58. Organic acids and possibly dry fallout contribution of potentially acidic substances, such as sulphate, may be responsible for the increased acidity. Nitrogen is the only nutrient which shows an overall decrease in concentration in throughfall and exhibits no obvious seasonal trend. As a constituent of proteins in the plant it is

more likely to be a product of decomposition than leaching (Frankland, 1976). Carlisle et al (1966b) believe that nitrogen in the form of nitrate and ammonium is probably taken up by microflora and plant surfaces, creating a net loss of the element in throughfall.

A noticeable feature of the throughfall plots is the peak which occurs in June 1981 for all ions, particularly ammonium, phosphate and potassium. This was attributable to the contamination of throughfall samples by frass produced by the larvae of Tortrix viridana and various other types of larvae which fed on the newly emerged oak leaves. The total nutrient input by frass in considered in the next section, but Figure 5.1 does show that this event provided a considerable nutrient input to the ecosystem.

Table 5.1 shows that ammonium and nitrite exhibit extremely high variance in weekly throughfall concentrations. The ions which also exhibit obvious seasonal trends, phosphate and potassium, also show high weekly variance. Table 5.5 gives the total (June 1980 - December 1981) nutrient inputs to the basin, in precipitation and throughfall and also the annual nutrient budgets for 1981. Throughfall chemistry was enriched by most of the ions monitored especially potassium, phosphorus and chloride. Total nitrogen was the only nutrient to experience a decrease in the original input.

5.2.0. Vegetation Morphology and Chemistry

In a forested ecosystem large quantities of nutrients are taken up from the soil and temporarily stored by trees and groundflora. The amount of nutrients which are taken up depends on the structure, type and age of the plant. The estimation of annual biomass accumulation and the determination of elements in samples, allows the calculation of nutrient

Table 5.5 **Total nutrient inputs June 1980 - December 1981 kg ha^{-1}**

	Ca	Mg	Na	K	NH_4	NO_3	NO_2	Cl	P
Rainfall	21.1	4.9	20.0	10.5	14.4	12.5	0.8	59.0	0.2
Oak throughfall	31.3	8.3	21.6	73.6	13.7	9.2	1.0	66.9	3.1
Bracken throughfall	30.9	8.9	24.7	95.5	12.2	8.3	0.8	93.4	2.8
Net gain/loss	9.8	4.0	4.7	85.0	0.8	-4.2	0.0	34.4	2.2

Total annual nutrient inputs 1981 kg ha^{-1} yr^{-1}

Rainfall	15.1	3.4	11.5	7.7	9.5	6.7	0.2	37.6	0.12
Oak throughfall	21.4	5.3	12.0	50.4	8.4	3.4	0.8	37.7	2.40
Bracken throughfall	21.4	5.3	16.4	66.9	10.0	3.5	0.5	48.2	2.00
Net gain/loss	6.3	1.9	4.9	59.2	0.5	-3.2	0.3	10.6	1.88

uptake from the soil. In this deciduous environment, nutrients are returned to the forest floor on an annual basis. Decomposition of litter releases the nutrients to the soil. Data concerning the chemistry of vegetation has been presented, using two different methods where possible. The percentage dry weight describes the relative amounts of nutrients in the vegetation sample over a period of time. This enables the importance of each nutrient in the plants growth or decay to be established. Nutrients have also been described in terms of biomass accumulation (kg ha^{-1}) and this provides an indication of the amount of nutrients taken up and returned to the soil throughout the year. Plotted values are mean weekly accumulations as a % dry weight for each biomass sampling period.

i) The young bracken plant is a sporophyte which originates from a prothallus. It spreads outwards over large areas by the continuous growth of its rhizome and root system. Three main types of rhizome were identified by Braid (1935) which overlie each other in the soil profile. The lowest form of rhizome in this study was found at 30cm depth and this type was responsible for invading the surrounding territory by extension of the terminal and bud. This leader rhizome produces occasional alternate side buds and in this soil grew upwards and then horizontally at approximately 15cm depth. These secondary branches were also seen to produce thin side growths which grew very near the soil surface. Each rhizome type produced long thin roots which radiated outwards in all directions; this fine network of roots proliferated in the L, F and H horizons and bound the organic matter together as a dense mat. Only the secondary and tertiary rhizomes produced fronds, with a single frond developing

from behind the terminal bud of each branch. If fronds were destroyed by frost or trampling they were replaced by subsidiary buds which normally lay dormant or developed the following year. Bracken fronds began to emerge in early May 1980 and in mid-April 1981 as a bent over rachis with tightly folded pinnae which gradually unfolded as growth commenced. The frond was entirely dependent on the rhizome for food reserves until the second pair of pinnae opened and photosynthesis began to supply food reserves. At the end of May the majority of fronds possessed at least two pairs of open pinnae and by July of both years the fronds were completely unfurled but the maximum height recorded of 1.95m was not achieved until September. The distribution of fronds over the hillslope was continuous with the exception of the hillslope base where the water table lay near the surface which limits growth (Poel, 1951). On the hillslope growth was influenced by the amount of light reaching the woodland floor and Burke (1953) also noted that bracken growth was more prevalent where the shade was less. Figure 5.2 illustrates the biomass accumulation of fronds and Figure 5.3 shows the biomass of the rhizomes throughout the study period. The fronds exhibit rapid growth in June and July of both years with maximum biomass occurring in October 1980 and in September 1981. Reduced growth occurred in the second year and this was probably due to frond damage by late April frost in 1981. The development of the subsidiary buds drained rhizome reserves and led to a lower total biomass production. Rhizome biomass in Figure 5.3 also shows a lower overall biomass in 1981. Three distinct peaks in the rhizome biomass can be seen, two of which coincide with the peak bracken biomass. At maximum productivity, the storage

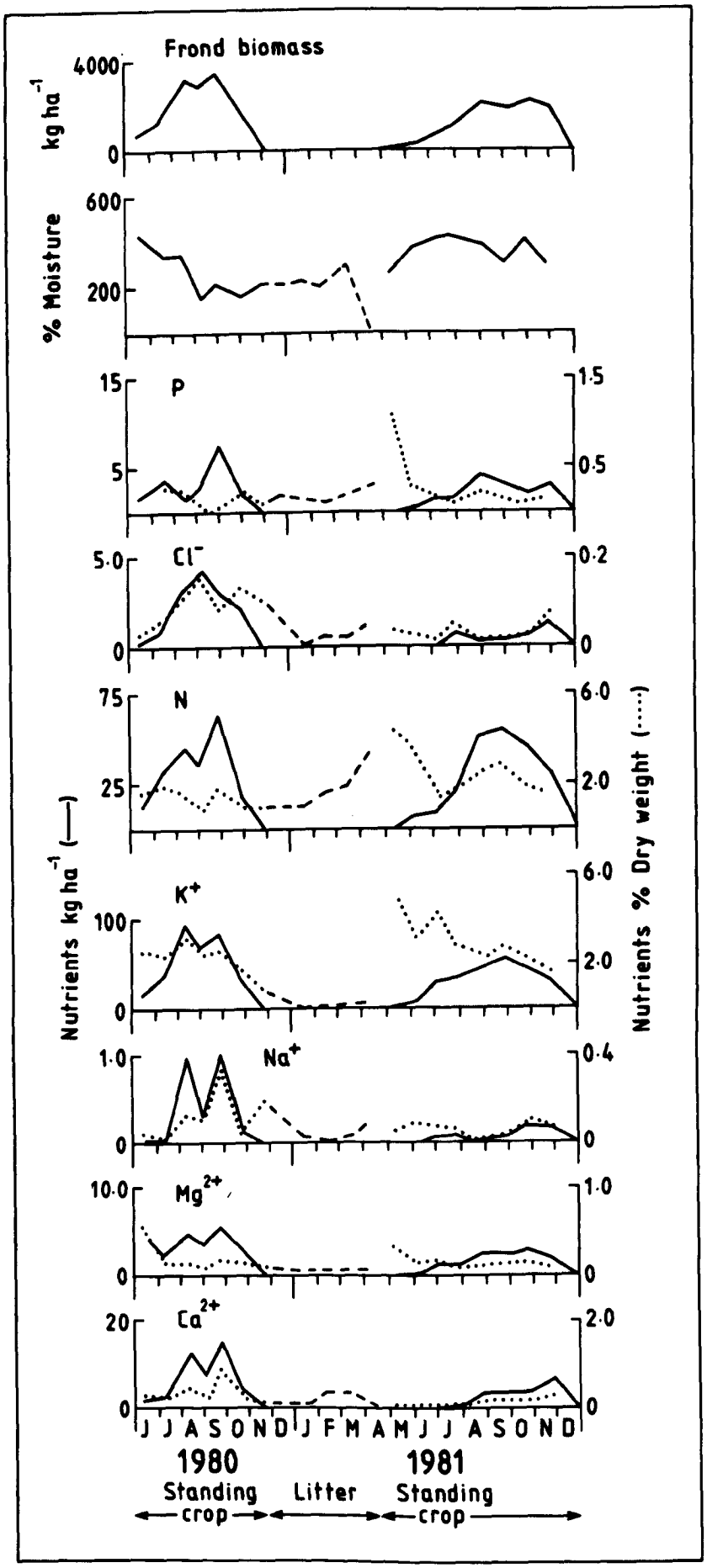


Figure 5.2 Frond chemistry

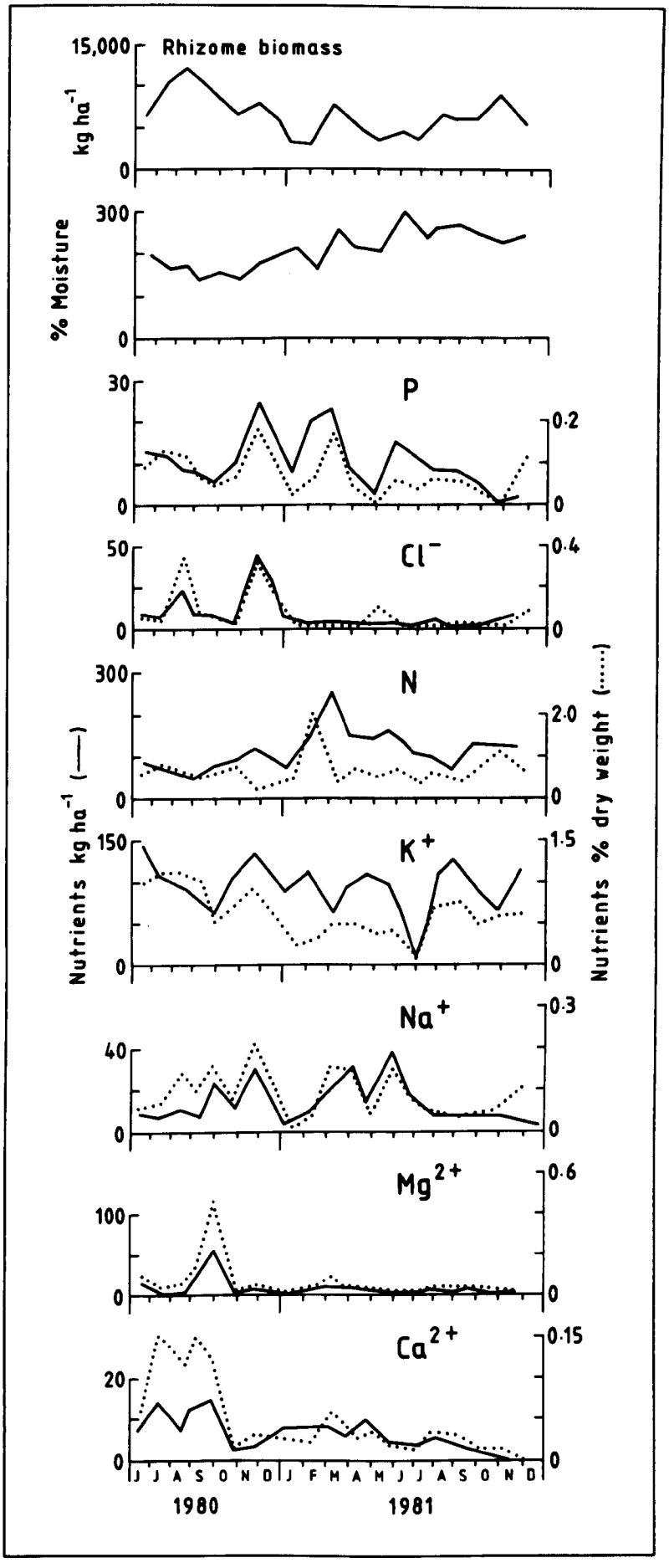


Figure 5.3 Rhizcme chemistry

organs are replenished with nutrients from the fronds and accelerated growth occurs whereby new territory is invaded. During the winter months the rhizome biomass falls considerably and this may be attributable to the expenditure of nutrients in preparation of the following years frond growth by the formation buds and the senescence of distal ends, though Callaghan et al (1981) found no significant seasonal trends. In spring, nutrient uptake by the rhizomes increased the biomass but during April and May 1981 frond emergence appeared to deplete the overall rhizome biomass, a phenomenon also observed by Hunter (1953). The deterioration of fronds became evident at the end of September of each year when the pinnules began to turn brown. By the end of October the majority of fronds were brown coloured but litterfall in the true sense could not occur as the bracken rachis remained erect. The total collapse of the frond was dependent on weather conditions which caused the rachis to eventually fold over. This event occurred in November 1980 and in December 1981.

Figure 5.2 illustrates nutrients as % dry weight of the bracken frond and also as nutrient accession (kg ha^{-1}) for each sampling period. When frond-fall occurred in November 1980 the sampling was continued and nutrient content is shown by the continuation of the plot through the winter months. The results compare with those of other workers, for example, Hunter (1944), Frankland (1976), Chen and Lindsey (1981) and Callaghan et al (1981). Potassium, nitrogen, phosphorus, magnesium and moisture content all have high values on emergence which decline through the growing period. Calcium, chloride and sodium follow the biomass

levels more closely by increasing their concentration in proportion to biomass. Cross correlation of the nutrients in the fronds as a % dry weight reveals few significant relationships with the exception of sodium with chloride and chloride with biomass. When frondfall occurs, nitrogen, calcium and phosphorus all increase as a percentage of dry weight, whilst potassium, sodium, magnesium and chloride decrease very quickly. This finding compares with the results of other workers, for example, Frankland (1976) and Chen and Lindsey (1981), who attribute the increase in nitrogen, calcium and phosphorus to adsorption of these elements from rainfall, frass and the surrounding litter. The remaining nutrients, particularly potassium are rapidly leached and Figure 5.2 shows that in January 1981 percentages are nearly zero. Table 5.6 summarises the characteristics of nutrients for fronds and rhizomes as a % dry weight. The accession pattern of nutrients in the fronds is generally the same as the biomass plot. Potassium, phosphorus and nitrogen are taken up more rapidly than other nutrients whilst magnesium, sodium and chloride only show small increases as biomass increases. Nitrogen, potassium and calcium all decrease in concentration more quickly than biomass and Callaghan et al (1981) attribute this factor to translocation of nutrients to the rhizomes. Figure 5.3 illustrates the nutrients in rhizomes. No nutrient in the rhizomes, except magnesium, correlates with those in the fronds despite the significant positive correlation of biomass, but comparison of graphs does show that as the concentration of nitrogen, potassium and phosphorus in the fronds increased a corresponding decrease was seen in the rhizome level. The cross correlation matrix for nutrients in the rhizome revealed few significant relationships;

Table 5.6 **Summary data for vegetation characteristics**

	Ca	Mg	Na	K	N	Cl	P	Moisture	Biomass
Fronds									
% dw $\bar{x}$	0.31	0.15	0.08	2.14	2.00	0.06	0.23	328.9	122.6
maximum	1.66	0.55	0.32	0.16	4.42	0.15	1.11	431.0	338.7
minimum	0.05	0.04	0.004	4.99	0.96	0.009	0.04	20.7	0.0
Rhizomes									
% dw $\bar{x}$	0.07	0.08	0.15	0.93	1.12	0.09	0.11	211.9	673.4
maximum	0.15	0.55	0.37	1.44	2.54	0.45	0.263	301.2	1368.9
minimum	0.01	0.02	0.02	0.18	0.48	0.001	0.008	140.7	314.15
SE	0.009	0.027	0.022	0.067	0.110	0.027	0.015	10.58	66.90
% C.V.	60.3	138.1	66.2	31.2	42.9	133.7	59.6	21.7	43.3

Continued..

Table 5.6 Continued

Oak	Ca	Mg	Na	K	N	Cl	P	Moisture	Biomass
% dw $\bar{x}$	0.39	0.16	0.11	0.79	2.35	0.03	0.16	82.7	-
maximum	0.89	0.81	0.17	1.58	5.08	0.07	0.42	128.4	-
minimum	0.05	0.05	0.0	0.07	0.97	0.007	0.03	21.2	-
Litterfall									
% dw $\bar{x}$	0.29	0.09	0.12	0.41	1.53	0.04	0.13	94.4	67.1
maximum	0.911	0.28	0.84	1.19	3.12	0.13	0.37	262.1	356.4
Litter									
% dw $\bar{x}$	0.15	0.04	0.10	0.36	1.4	0.05	0.13	219.9	5608.0
maximum	0.82	0.19	0.69	1.33	3.00	0.12	0.33	366.1	9236.7
minimum	0.006	0.007	0.01	0.14	0.83	0.0	0.06	107.8	3694.0
SE	0.04	0.01	0.04	0.06	0.11	0.008	0.02	15.3	570.9
% C.V.	122.3	107.1	152.9	68.1	33.7	70.6	53.2	30.3	44.4

calcium correlated with magnesium and moisture content, whilst sodium correlated with nitrogen. The lack of correlations of nutrients in the fronds and rhizomes may reflect the independent roles which each nutrient plays in the physiology of the plant. As % dry weight calcium and magnesium have similar contents in the fronds and rhizomes, the fronds have more potassium and nitrogen whilst the rhizomes contain the most sodium, chloride and phosphate. Sodium and chloride play limited roles in the physiology of a plant and whilst the uptake of these elements by rhizomes is not selective it would appear that they are not translocated to the aerial parts of the plant.

ii) Oak and litterfall

The oak trees on the hillslope were originally planted as part of a large landscaping scheme c.1840. Their condition on the hillslope was poor, several dead, branchless trees remained standing and all other trees were stagheaded. Examination of the increment core and trunk section revealed very narrow annual rings which often merged, suggesting poor growth and, indeed, few trees had girth measurements which exceeded 200cm. During the week commencing 15th April 1981 a large oak tree was felled by strong winds to reveal an extremely shallow rooting depth of approximately 0.5m despite the 20.2m height of the tree. This particular tree had rooted to a depth just above the winter water-table and where the water-table did lie near the soil surface no tree had a girth exceeding 100cm.

Bud break of the oak occurred after bracken emergence and in the second week of May 1980 small green leaves emerged accompanied by litterfall consisting of budscales. This event occurred in the first week of May 1981 and in both years the trees were quickly partially defoliated by the larvae of Tortrix viridana and the larvae of various unidentified fly species. Calculation of defoliation losses, by the Carlisle et al (1966a) method showed that 50.1% of the oak leaves were consumed and a considerable amount of frass was produced over a five week period reaching a maximum in the first week of June. An approximate calculation of the amount of frass produced was made by collecting frass on a sheet for one week and over a five week period 425kg ha^{-1} of frass was calculated to have fallen onto the woodland floor. A secondary flush of leaves appeared in late June and early July. Clearly, if this defoliation occurred on a regular basis over a period of time it may partially account for the poor annual growth of the oak as nutrient reserves are continuously drawn upon. It was noticeable, however, that only a very small amount of defoliation occurred in June 1982 and this was probably attributable to the severe winter of 1981/82 destroying the insects. Oak litterfall was characterised by a period of abscission in autumn of both years and an equally large amount of litter was input after a storm event when small branches were removed from the trees in April 1981. Figure 5.4 plots the litterfall biomass. The total amount of leaf fall in the autumn provides an estimate of the annual production of oak and Table 5.7 compares values for 1980-81 with those of Carlisle et al (1966b), for a variable aged oak woodland in Grizedale Forest and for a mixed hardwood forest in Hampshire, U.S.A. (Gosz et al, 1972).

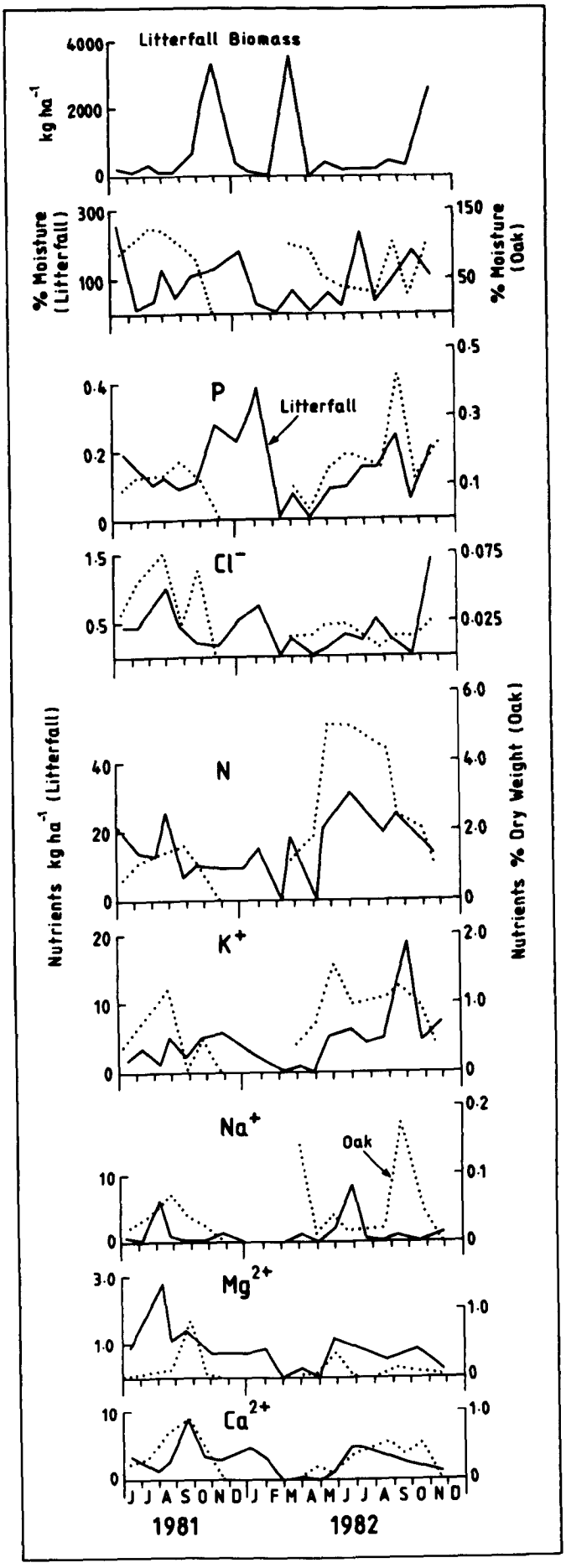


Figure 5.4 Litterfall, oak leaf and twig chemistry

Table 5.7 **Comparison of total tree litterfall in deciduous forests**

		kg ha^{-1}
Monks Park Wood -	May-December 1980	5206.8
	1981-82	7586.0 (4022.0 + 3564.0 branches)
Grizedale Forest*		3857.8
Hubbard Brook**		5702.0

* Carlisle et al (1966b)
** Gosz et al (1972)

The Monks Park Wood figures fall within the range proposed by Bray and Gorham (1964) for deciduous forest production. Few studies consider the contribution that ground flora makes to total litter accession rates (Walsh and Voigt, 1977). An additional 3386.5 and 2300.0kg ha^{-1} of bracken fronds were added to the forest floor in 1980 and 1981 respectively at Monks Park Wood. Therefore total litterfall and frond-fall is in the range of 8500-9900kg ha^{-1} for this catchment.

The nutrient levels in oak leaves and twigs are presented as % dry weight for the periods when buds or leaves were present (Figure 5.4), consequently the plots for each nutrient are very similar to those of the bracken fronds. Nitrogen and phosphate were taken up rapidly in May/June of each year with nitrogen reaching a maximum (5.08% dry weight) in May 1981. Chloride percentages show peaks in August and October 1980 but were comparatively constant in 1981. Calcium and potassium were taken up fairly slowly and reached peak levels in August/September. Sodium levels were low in comparison to other nutrients but did increase during 1981. Phosphorus and

nitrogen exhibit a fall in % dry weight in September which occurred before the main period of leaf fall. Comparison of oak with % dry weight of bracken fronds shows that oak leaves and twigs contain more nitrogen and sodium but the remaining nutrients are more prevalent in the bracken fronds.

The input of nutrients to the litter layer by oak litterfall was not completely controlled by the dry weight of litterfall. Figure 5.4 shows that peak nutrient inputs (kg ha^{-1}) did not always coincide with maximum biomass. This discovery emphasised the role of small, nutrient rich, litter fractions such as budscales, flowers and frass. The accession of nutrients to the soil from oak leaf-fall was low, particularly for calcium, magnesium and potassium and this supports the hypothesis that nutrients may be translocated to other parts of the tree prior to abscission. Nutrients are also lost by leaching from the tree canopy at this time. The sodium and chloride content of litterfall was very low, whilst nitrogen and potassium were the most abundant nutrients. In April 1981 litterfall consisted of branches and, despite the large biomass input, it can be seen that the actual nutrient content was low. Table 5.6 shows that the amount of nutrients in oak litterfall as a % dry weight was less than the nutrient content of the growing oak twigs and leaves. When litterfall occurs, nutrients have either been previously translocated to storage organs or leached from the leaf surface.

iii) Litter

Biomass was estimated from the litter sampling but the variance for each week was very high and therefore all nutrient values are

presented as a percentage of dry weight only and no seasonal biomass is presented. The mean biomass value of 56070.0kg ha^{-1}, calculated from all samplings, is tentatively suggested to give an approximate value of the decomposition cycle assuming there is no overall accumulation of litter, thus:-

Equation 1

		kg ha^{-1} yr^{-1}
Store of litter S	=	56070.0
Accession rate of litter A	=	9500.0
Decomposition cycle	=	S/A

therefore a 5.9 yr decomposition cycle was required to retain an equilibrium. Decomposition studies are lengthy and involve the continuous monitoring of litter decay for many years. Frankland (1976) estimated that 95% of frond decomposition would occur only after 11-23 years with the time depending primarily on the rate that fronds were incorporated into the litter and secondly on the soil conditions. This slow rate of decomposition is comparable with those of woody plants with similarly high lignin contents, for example, oak twigs and branches. In comparison, the decomposition of oak leaves and buds was rapid and investigation revealed few intact leaves in the litter layer in the spring and summer months. Bocock and Gilbert (1957) calculated a 23% loss in dry weight of the leaves of Quercus petraea after only six months. In Monks Park wood the decomposition of oak leaves was probably dominated by litter feeding arthropods as no earthworms were found and fungal decay was assumed to be too slow to account for the rapid disappearance of the oak leaves.

Figure 5.5 gives the nutrients as a % dry weight in litter. Chemical analysis of the frond litter from 1980 growth showed significant increases or decreases in nutrient percentages. However, the analysis of the total litter did not provide such obvious changes. The litter sample consisted of a heterogeneous mass of organic particles in various stages of decomposition. Significant changes in nutrient concentration were attributable to periods of litterfall, accelerated decomposition and leaching. Calcium, magnesium and chloride all show peaks in mineral accession during the main leaf-fall periods. Phosphorus, potassium, nitrogen and magnesium show increases in April when biological activity commences, but nitrogen percentages fall in summer and this trend may be attributable to uptake by the fine bracken roots or by microbial release to the atmosphere. All percentages of nutrients in the litter are lower than in the growing vegetation with the exception of sodium and chloride which remain at similar levels throughout the different vegetation samples. The lower values of other nutrients are attributable to decomposition losses and leaching. Frankland (1976) states that leaching of nutrients from litter is an important factor in decomposition. Various workers, for example Gliessman and Muller (1972) and Lodhi (1978) report that decaying bracken litter has an allelopathic potential, which in this woodland may be responsible for the absence of other ground flora on the hillslopes.

5.3.0 The Soil

The soil is a dynamic medium varying in its physical and chemical properties over time and space. This dynamism is difficult to identify

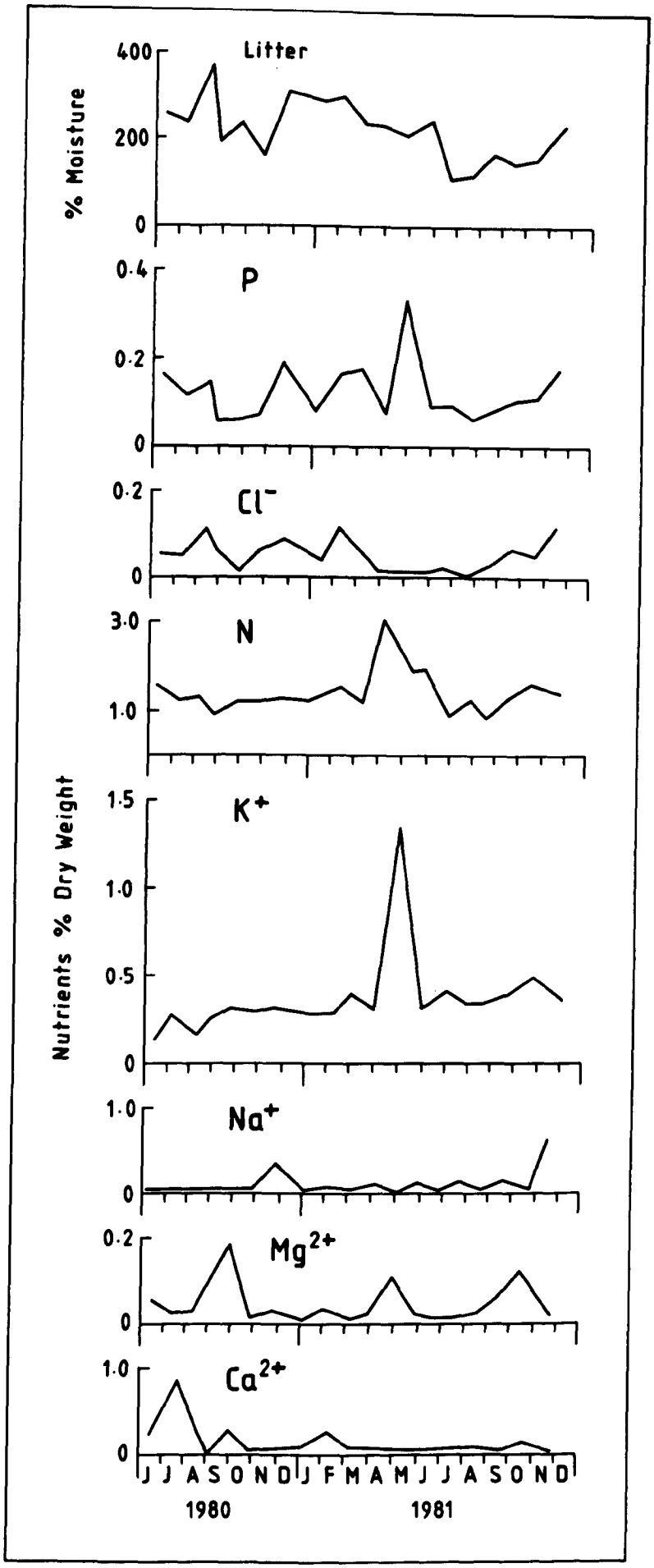


Figure 5.5. Litter chemistry

with any degree of accuracy; intensive sampling is site destructive and insufficient samples do not permit identification of the natural variation of properties which exist (Ball and Williams, 1968). The present study was further complicated by the occurrence of a variety of soil series in the drainage basin and the presence of two distinct soil types on the instrumented hillslope. Soil and soil water chemistry is dependent on a large number of physical and chemical properties of the soil. The physical characteristics of the soil which affected soil water retention and conductivity were discussed in Chapter 4.0 and this section describes some of the soil chemical properties which affect solute and nutrient concentrations in the pedosphere.

Cation exchange capacity (C.E.C.) is a measure of the ability of a soil to hold cations in exchangeable form. It is a property of the fine soil particles, particularly clays, and the organic matter in the soil. The external surfaces of clay and organic matter are negatively charged and attract and hold positively charged cations. The adsorbed cations may then be taken up directly by plant roots or leached from particle surfaces by percolating water (Curtis et al, 1976). In the latter case cations such as calcium, magnesium, sodium and potassium are replaced by hydrogen ions.

The type and relative proportions of clay minerals in a soil help to explain the C.E.C. of the different soil horizons and Table 5.8 gives the results of the semi-quantitative clay mineralogical analysis. The range of percentages for each clay type are relative to each other and the classification of mineralogy was made in conjunction with the C.E.C. and non-exchangeable potassium (K_2O) content of clay minerals, described by Avery and Bullock (1977). C.E.C. is used as an index of expansible layer

content in clay particles and hence the type of clay present can be deduced whilst K_2O values are an index of mica content. Values for K_2O were obtained from Whitfield and Beard (1980) and were 2.8, 2.7 and 2.2% for the Ah, Bt(g) and BCg horizons respectively (Table 5.9).

Table 5.8 **Soil chemical characteristics**

Horizon	Ah	Bt(g)	BCg
Depth cm	10-16	16-56	56-140
Organic Carbon %	5.7	1.0	1.93
pH in water (1:2.5)	3.7	4.15	-
pH in 0.01 $CaCl_2$ (1:2.5)	3.05	3.25	-
C.E.C. me 100 g^{-1}	27.8	10.4	6.04
Kaolinite	25-50%	50%	10-25%
Mica	25-50%	25-50%	50%
Chlorite	10-25%	10-25%	5-10%
Smectite	5-10%	5-10%	10-25%
Mineralogy class	mixed	kaolinitic	mixed
Total N % dry wt	0.099	0.045	0.013
Total P % dry wt	0.03	0.009	1.5^{-03}

The Ah and BCg horizons both have mixed clay mineralogies though the relative amounts of each mineral is different. In the A horizon there are equal quantities of kaolin and mica with very little smectite. In the BC horizon the dominant mineral is mica and there is a greater proportion of smectite. The B illuvial horizon is dominated by kaolinite and has a very small proportion of smectite. C.E.C. values are low in the subsoil and

illustrate the absence of significant quantities of expansible clays such as vermiculite and montmorillonite whilst the distribution of clay types reflects the process of weathering in this soil profile. Illite, chlorite and smectite are products of leaching in the early stages of weathering and in the later stages kaolinite replaces the former minerals (Grim, 1962). The proportions of clay minerals in this soil indicate a well weathered profile with a low C.E.C. The presence of an argillic horizon confirms the translocation of clay minerals by leaching.

Table 5.9 **Properties of Clay Minerals**

Clay mineral	C.E.C.	K_2O
	me $100g^{-1}$	%
Kaolinite	3 - 15	3.5
Mica (illite)	10 - 40	7.0
Chlorite	10 - 40	-
Smectite (montmorillonite)	80 - 150	-

In this soil the clay minerals identified have a low exchange capacity (Table 5.9) and therefore organic matter must account for a significant part of the C.E.C. especially in the A horizon. Foster and Grieve (personal communication) found a highly significant correlation between C.E.C. and organic carbon content in this catchment. The high A horizon value of 27.8 me $100g^{-1}$ is a reflection of the humose nature of the soil whilst both the B and BC horizons have low C.E.C. despite the increased montmorillonite content in the B horizon.

Oxidizable organic carbon in the soil occurs as plant or animal matter, the immediate products of decomposition and also as humus. Organic matter affects the physical properties of the soil by retaining moisture and improving structure. Chemical properties are also enhanced, raising C.E.C. and increasing the amount of available plant nutrients. Carbon compounds within the soil are in a continuous state of flux: additions are in the form of dead organic material and also as leaching products in throughfall. Section 5.2.0 (iii) described organic matter input by litterfall. Dissolved organic matter concentrations in throughfall reached levels as high as 56.7kg ha^{-1} wk^{-1} (Foster and Grieve, 1982). The main loss of carbon in this soil is probably by carbon dioxide evolution and to a lesser extent by leaching loss of carbonic acid. Foster and Grieve (1982) show that only 1% of dissolved organic matter input was lost from this ecosystem in streamflow. The A horizon is defined as humose by the relationship of organic carbon content with the percentage of clay in the soil (Hodgson, 1974) and has a moderately large mean value of 5.7%. Under very acid conditions mobile organic compounds are formed and these may be leached out and precipitated in the B horizon (Russell, 1961). The organic carbon content in the BC horizon may be attributable to this phenomenon as it was greater than the overlying B horizon.

Foster and Grieve (personal communication) showed that there was a pronounced seasonal trend in organic carbon content in the top 10cm of mineral soil sampled at site 1 between 1978 and 1980. They found that maximum levels occurred in winter and summer with minimum levels in spring. The data for 1980-81 of this study also showed summer maxima, increasing from low winter and spring levels. Figure 5.6 shows that the B horizon concentrations were fairly constant, whereas accentuated peaks can be seen in the A horizon during May 1981 and July 1981. Foster and Grieve found a close relationship between carbon content, C.E.C., soil moisture and soil temperature. Table 5.10 shows that a significant negative correlation between carbon and moisture exists in this study, that is soil carbon levels decrease with increasing moisture content. This is probably related to the leaching and translocation of humus to lower horizons by percolating water. Table 5.10 shows no significant correlation between carbon and the individual exchangeable cations in the soil in either soil horizon and inspection of the plotted data revealed a wide scatter of points within the axes. Other cations such as iron, manganese or aluminium may be responsible for a large proportion of the C.E.C. Values of 3.8 and 3.4mg l^{-1} of manganese and iron respectively have been measured in the soil solution at site 1.

The influence of soil temperature on the dissolved organic carbon content of the soil is indirect; as soil temperature rises the activity of soil organisms will increase and mineralisation of litter will be more rapid providing there is sufficient moisture present (Russell, 1961). The seasonal input of organic carbon by litterfall is of little importance in explaining soil carbon levels because decomposition processes must initially operate to incorporate the carbon into the mineral soil. Dissolved organic matter contributions in throughfall may be more important especially during bud break, senescence and when frass contaminates the sample.

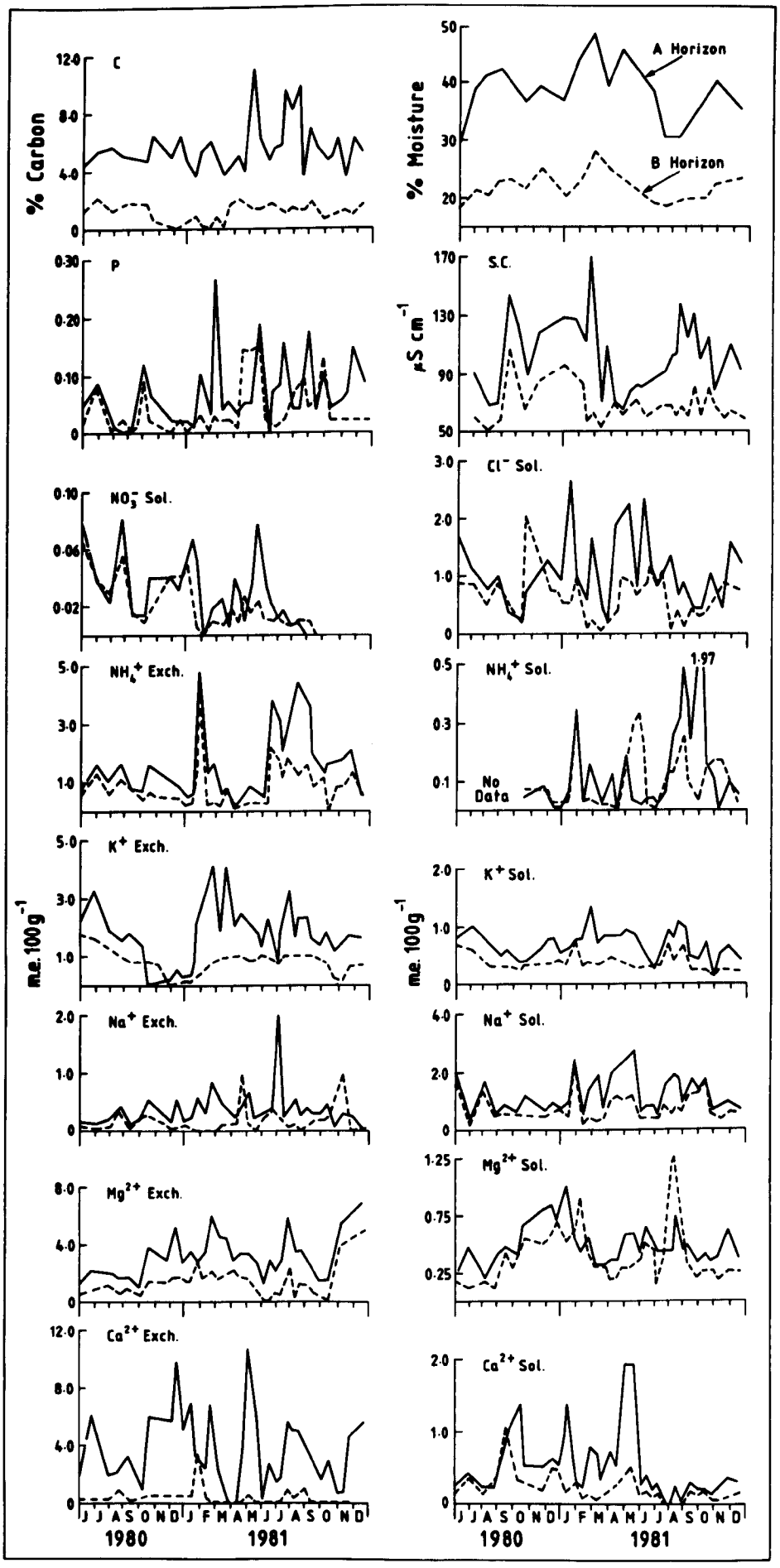


Figure 5.6 Soil Chemistry

Table 5.10 **Cross correlation matrix for variables in the A and B horizons**

A Horizon

	Mois	Carb	ECa	EMg	ENa	EK	ENH_4	CaS	MgS	NaS	KS	NH_4S	NO_3	Cl	P	Sc
Mois																
Carb																
ECa	+															
EMg	+															
ENa																
EK																
ENH_4																
CaS			+				-									
MgS			+			-		+								
NaS								+								
KS			+			+				+						
NH_4S																
NO_3			+			-	-	+	+							
Cl			+						+							
P																
SC	+					+	+		+		+					+

B Horizon

	Mois	Carb	ECa	EMg	ENa	EK	ENH4	CaS	MgS	NaS	KS	NH_4S	NO_3	Cl	P	Sc
Mois																
Carb	-															
ECa																
EMg																
ENa					+											
EK			+													
ENH_4	-		+			+										
CaS	+															
MgS		-	+													
NaS			+			+	+									
KS						+										
NH_4S			+			+	+				+	+				
NO_3						-		+								
Cl								+						+		
P																
SC						+					+			-	-	

+ significant positive correlation

- significant negative correlation

The acidity of soils in oak woodland ranges from pH 3.8 to 5.0 (Pearsall, 1952). A pH of 3.7 in the A horizon of the hillslope is therefore very low and is only slightly less acid (pH 4.15) in the subsoil (Table 5.8). The soil pH in 0.01 M calcium chloride is lower and probably gives a more realistic representation of the pH around plant roots (Russell, 1961). This is because the calcium concentration approximates to that of the soil solution and little cation exchange between the soil and water will occur during measurement. The acidity is probably attributable to leaching which leaves the soil horizons base deficient; the process is accelerated by the addition of humic acids from the L, F and H layers.

Nitrogen and phosphorus are the essential plant nutrients which are normally the limiting factors to plant growth. Determination of the total amount of nitrogen and phosphorus in the soil provided an indication of potential nutrient deficiencies. The average amount of total soil nitrogen under a humid forest ecosystem is approximately 0.1% of soil dry weight (Black, 1968) and this is comparable with 0.099% in the Ah horizon (Table 5.8). The percentage is smaller in the lower horizons and Hesse (1971) attributes this to the fact that the majority of nitrogen in soil is organically derived and occurs near the soil surface. The total content of phosphorus in soils is generally low and most soils contain between 0.022 and 0.083% of soil dry weight. The percentage of total phosphorus in the A horizon (0.03%) falls within this range, however the subsurface horizons are deficient in phosphorus.

Soil temperatures closely followed those of air temperatures and exhibited a significant correlation at the 99.9% level for 76 samples at both the 4cm and 8cm soil depths. The minimum temperature recorded was 2.6^{o}C in February 1981 at 4cm depth and the maximum temperature was 15.5^{o}C

in August 1980 also at 4cm. The minimum critical temperature for plant growth is $6^{o}C$ and soil temperature reached this level in the first week of April 1981. Soil temperature did not fall below $6^{o}C$ until the first week of December in both years. Temperatures did not fall below zero at any time because of the mulching action of the litter layer which minimised heat loss and prevented frost penetration. The moisture content of the soil also influences soil temperature; as water is removed from a soil horizon, by drainage or evapotranspiration, incoming radiation will be used to heat soil and air rather than to evaporate water (Russell, 1961). Soil temperature is important in this study as the rate of mineralisation and the release of solutes from organic matter is increased by rising temperatures.

5.3.1. Spatial variation in soil chemistry

A major problem of any ecological investigation is the variation in soil characteristics which occur within the study area. Ball and Williams (1968) state that the purpose of soil analysis is to make meaningful statements about the properties of a relatively large soil area from laboratory determination on small samples. In this study sampling was confined to the Melbourne soil series on the hillslope and Table 5.11 gives the percentage coefficient of variation and 95% confidence limits for each variable which was determined in the spatial variability test. Beckett and Webster (1971) provide a comprehensive review of soil variability and they found no recommendation for a maximum acceptable variance in soil properties. Generally, values between 10 and 30% have been identified in work which attempts to describe seasonal variation, for example Ball and Williams (1968) and Grieve (1980). Table 5.11 shows that the majority of variables have a percentage coefficient of variation lower than 30% in the

Table 5.11 **The spatial variability of the hillslope soil**

	% Mois	% Carb	me $100g^{-1}$ ECa	EMg	ENa	EK	ENH_4	CaS	MgS	NaS	KS	NH_4S	NO_3	Cl	P	SC	Total $\bar{x}$ % CV
Horizon A																	
$\bar{x}$	35.0	4.2	2.9	3.9	1.3	1.4	2.6	0.1	0.3	1.3	0.5	0.3	0.05	0.8	0.01	113.0	
%CV	10.1	16.3	49.0	19.9	73.1	14.7	16.6	10.7	37.9	29.4	23.9	4.4	19.1	8.6	17.5	11.9	22.7
$CI_{\pm}$	4.08	0.93	1.09	0.85	1.41	0.25	0.43	0.07	0.11	0.42	0.13	0.14	.01	0.08	1.5^{-4}	15.3	
Horizon B																	
$\bar{x}$	16.2	1.8	0.1	2.0	0.1	0.7	1.6	0.1	0.3	0.9	0.2	0.2	0.03	0.91	.008	86.3	
%CV	11.5	12.2	51.1	33.2	65.2	39.7	14.0	23.3	24.2	35.6	34.8	45.0	31.1	47.3	62.7	19.8	34.4
$CI_{\pm}$	2.1	0.41	0.06	0.76	0.07	0.29	0.25	0.06	0.08	0.36	0.09	0.11	0.01	0.5	1.9^{-4}	19.7	

number in sample = 6

E = exchangeable

S = water soluble extract

A horizon. However, the B horizon is far more variable and this phenomenon was also observed by Webster and Beckett (1971) in their studies. These values may also incorporate the analytical variability described in Chapter 3.0, which arises from the heterogeneity of a subsample and analytical error. No correction to soil data can be made for spatial variability but the application of 95% confidence interval (C.I.) to soil data collected over the study period would identify the variations not attributable to site variability (Table 5.11).

Frankland et al (1963) found that seasonal variation in soil properties was masked by the large spatial variability of the study site and Ball and Williams (1968) reported similar findings. Table 5.12 presents the descriptive statistics for soil properties which were determined over the entire study period. A comparison of the %CV in Table 5.11 and 5.12 for each variable, show that only two parameters exhibit less seasonal variation than the overall site variability. The remaining variance probably can be attributed to seasonal variation in soil properties.

5.3.2. Seasonal variation in soil chemistry

All soil nitrate is held in the soil solution whilst ammonium may also be held in the exchangeable form. The majority of nitrogen is derived from the mineralisation of organic matter and this process is normally carried out by nitrifying bacteria. In acid forest soils mineralisation of organic matter by bacteria and soil fauna such as earthworms is decreased and the process is performed by soil fungi. Fungi are less efficient than bacteria and therefore the rate of mineral release is tightly regulated by the high lignin content of bracken litter, soil acidity and the formation of clay humus complexes. McLaren and Peterson (1967) state that only 1-3% of organic nitrogen is released during each growing season and in this soil a

Table 5.12 **Descriptive statistics for seasonal properties of the soil**

me $100g^{-1}$

	% Mois	% Carbon	Exchangeable Ca	Mg	Na	K	NH_4	Soluble Ca	Mg	Na	K	NH_4	NO_3	Cl	P	SC
Ah																
$\bar{x}$	45.2	5.7	3.88	3.58	0.42	1.78	1.64	0.47	0.51	1.33	0.71	0.18	0.02	1.45	0.07	100.1
maximum	58.2	10.9	10.72	6.74	1.98	4.12	4.91	1.9	1.01	2.70	1.40	1.97	0.08	10.7	0.26	171.0
minimum	30.3	3.5	0.0	1.36	0.08	0.04	0.0	0.0	0.29	0.52	0.98	0.0	0.0	0.13	0.0	64.0
% cv	14.9	32.3	69.3	40.6	82.1	59.5	80.0	102.1	35.0	50.4	37.2	205.5	116.7	130.0	87.1	24.9
Btg																
$\bar{x}$	21.7	1.0	0.36	1.61	0.30	0.72	0.83	0.17	0.39	0.78	0.42	0.10	0.2	0.62	0.06	62.7
maximum	24.7	2.0	3.38	4.92	2.69	2.03	4.9	0.51	0.87	2.49	1.72	0.34	0.11	1.97	0.28	83.0
minimum	19.0	0.02	0.0	0.0	0.0	0.03	0.0	0.0	0.17	0.26	0.17	0.01	0.0	0.09	0.0	50.0
% cv	6.4	55.0	182.9	75.8	176.8	60.9	116.1	83.3	44.9	61.5	67.8	99.0	146.6	67.4	123.3	24.1

number in sample = 29

maximum of 4% of the total nitrogen was held in the soil solution as nitrate and ammonium. Trudgill et al (1981) state that nitrate is highly soluble and is readily leached, whilst Russell (1961) reports that ammonia can be lost from the soil surface by volatilization.

Figure 5.6 shows that nitrate and ammonium appear to be related in their occurrence. In January 1981 nitrate levels fall and ammonium concentrations rise whilst the opposite occurs in the following spring months. In autumn/winter of 1981 no nitrate could be detected but ammonium levels rose considerably. Table 5.10 shows no significant correlation between the ions but the relationship may also be attributed to the effects of temperature and soil water status controlling the rate of nitrification. Likens et al (1977) noted that nitrate concentrations increased after a period of soil freezing. Nolan (1982) showed that alternate wetting and drying of soils from this catchment gave rise to a decrease in nitrate content but an overall increase in total nitrogen. This indicates that ammonium increases over time during wetting and drying cycles at the expense of nitrate levels. The activity of soil fauna is mainly responsible due to the production of ammonium-nitrogen from organic nitrogen in the initial stage of decomposition. This process only provides a partial explanation for the levels of water soluble nitrate levels. The diluting effect of percolating water may be responsible for the low levels detected in February 1980 and autumn/winter 1981.

Plants are unable to absorb phosphate directly from organic phosphorus compounds in the soil and therefore rely on the immediately available inorganic form of phosphorus which occurs almost entirely as orthophosphate in the soil solution (Hesse, 1971). The amount of orthophosphate present in the soil solution at any point in time is low and

therefore it is the rate of replacement which is of interest. The main source of orthophosphate is organic matter and the rate of decomposition is an important factor determining availability. Cruickshank (1977) states that approximately 80% of the total phosphorus is stored in the organic matter content of the soil and Figure 5.6 shows that extractable phosphorus is greater in the A horizon. However, the amount of available phosphorus in the A and B horizons is less than 10% of the total phosphorus in the soil. In the Ah horizon most of the total phosphorus is stored in the organic matter, but in the mineral B horizon orthophosphate is probably rendered insoluble by precipitation as hydroxy-phosphates of aluminium, iron and manganese, which are known to exist in the soil solution in significant quantities in Monks Park wood, for example

Equation 2

$$Al^{3+} + H_2PO_4^- + 2H_2O \longrightarrow 2H^+ + Al(OH)_2H_2PO_4$$

soluble — insoluble

The insoluble compounds must be weathered or the orthophosphate can be removed by anion exchange, for example by the hydroxyl ion, to return to the soluble state. Precipitation by the high concentrations of iron and aluminium is likely to predominate in this acid soil and only very small quantities of phosphorus are therefore available to plants in the soil solution. No obvious seasonal trend in phosphorus concentration can be seen in the A or B horizons and phosphorus does not correlate with any other measured variable in the soil (Table 5.10). Russell (1961) states that the phosphorus concentration in the soil solution remains fairly constant and is not dependent on soil moisture status. Whilst microbial activity and mineralisation of organic matter are seasonal phenomena no

evidence of the subsequent increase in the release of orthophosphate could be identified, this occurrence may be due to the immediate immobilisation of phosphorus by chemical precipitation.

Chlorine occurs as chloride in soils and, with sulphur, is one of the dominant anions in the soil solution. It is an essential plant micronutrient, being an important osmotic regulator, but there is little literature on its behaviour in the soil. Chloride forms simple soluble salts, for example, potassium chloride, which are easily removed from soil horizons by leaching. Consequently chloride levels in the soil solution are generally low with concentrations ranging between 0.001-0.1% of the total soil dry weight (Buckman and Brady, 1971). Ericksson (1960) states that the amount of chloride present in any soil cannot be accounted for by weathering of soil particles and that precipitation supplies chloride in considerable quantities. Figure 5.6 shows that during the autumn/winter months chloride concentration rose in both horizons corresponding with chloride increases in frontal rainfall. There is, however, no significant linear correlation between rainfall and soil solution chloride concentrations. Figure 5.6 shows that in summer, levels were also high and this was attributed to evaporation and subsequent concentration of chloride inputs. In October of 1980 and 1981 chloride levels in both horizons fall and this may have been due to an initial flushing effect (Nortcliff and Thornes, 1978). Cross correlation of other nutrient concentrations with chloride in the soil reveals the form in which chloride is held in the soil solution and illustrates its disassociation with sodium. Table 5.10 shows few significant correlations, with chloride only correlating with water soluble magnesium, exchangeable calcium in the A horizon and water soluble calcium and nitrate in the B horizon. As one of the most abundant anions in the soil solution, chloride has preferential attachment to the free

radicals of cations which are not easily leached from the soil. The divalent cations, calcium and magnesium, are therefore more likely to combine with chloride at the exchange sites and in the soil solution.

ii) Exchangeable and water soluble cations

Available cations may be held in two forms in the soil matrix, that is, on the exchange sites of the clay humus complex and dissolved in the soil solution. The amount of cations in solution or on exchange sites cannot be considered in isolation as the relative proportion of each is interdependent and is controlled by the prevailing soil conditions. In this acid soil hydrogen was tightly bound to exchange sites giving a low pH, and removal by other cations was unlikely unless the hydrogen ion was outnumbered by another cation on an equivalent basis - the law of mass action (Buckman and Brady, 1971). Different cations have different powers of replacement and after hydrogen the order of replacement is usually calcium > magnesium > ammonium potassium > sodium. Table 5.13 shows that this is the order of exchangeable cation abundance in the A horizon. In the B horizon the order is different, magnesium > ammonium potassium > calcium > sodium. The larger amount of magnesium may derive from the higher micaceous clay content of that horizon and the subsequent production of constituent cations by weathering of that clay mineral.

Examination of exchangeable and soluble cation ratios in Table 5.13 reveals that calcium, magnesium and ammonium are present in greater amounts as exchangeable ions. Slightly more potassium ions are held in the exchangeable form than soluble,

Table 5.13 **Summary of Exchangeable Cation Characteristics**

	Ca	Mg	Na	K	NH_4	C.E.C.	Total%
Horizon A							
me $100g^{-1}$ $\bar{x}$	3.9	3.6	0.4	1.8	1.64	27.8	
% of C.E.C.	14.0	12.9	1.4	6.5	5.9		40.1
Exch: sol ion ratio	8.3	7.0	0.3	2.5	9.1		
*Rating	low	high	mod	v.high	-		
Horizon B							
Me $100g^{-1}$ $\bar{x}$	0.4	1.6	0.3	0.7	0.8	10.4	
% of C.E.C.	5.8	15.4	2.9	6.7	7.7		36.5
Exch: sol ion ratio	2.1	4.1	0.4	1.7	8.3		
*Rating	v.low	mod	low	mod	-		

* Curtis, Courtney and Trudgill (1976).

whereas more sodium ions are present in the soil solution than on exchange sites. The relative proportion of each type of cation is dependent on the soil moisture status but the relationship is not simple. Russell (1961) describes the relationship by means of The Ratio Law, whereby an increase in moisture content does not disturb the ratio equilibrium, provided the activities of the monovalent cations are decreased by one ratio and those of divalent ions in the square of that ratio. The implication of this law being that in a soil which has cations of mixed valency in an equilibrium state, an addition of water will result in ions of a higher valency being taken up from the solution thus displacing weakly bound monovalent ions. Russell points out that monovalent cations are stronger extractors of exchangeable cations as a direct consequence of the ratio law. One would therefore expect an inverse relationship to exist between exchangeable and soluble ion concentrations. Table 5.10 shows that a positive linear relationship exists between soluble and exchangeable potassium in both horizons, calcium in the A and ammonium in the B horizons, but no inverse relationships were found. However, it is difficult to generalise the relationship between soluble and exchangeable ion concentrations as the equilibrium state is constantly changing and difficult to determine.

The calcium in soil is normally derived from primary minerals and XRF analysis showed calcium to be a major component of shale and sandstone in the area. Calcium is normally the dominant cation in the soil solution (Hesse, 1971) but in acid soils can be deficient. Table 5.13 gives the ratings for each exchangeable cation as defined by Curtis et al (1976). Black (1968) states that

at least 30% of the C.E.C. must be accounted for by calcium for a plant to grow normally, but the actual value in this study was only 14%. Figure 5.6 shows that calcium concentrations in the B horizon were low for exchangeable and soluble ions but both forms follow the trends of the A horizon. Autumn/winter peaks are seen with a maximum value in May 1981 and Table 5.12 shows the seasonal variance for this ion to be high.

Magnesium is probably derived from the weathering of clay minerals and the rate of release is inversely proportional to particle size. Black (1968), for example, reports that 50% of magnesium was held in the 20um fraction, thus the soil texture influences availability. Magnesium follows a similar pattern to calcium with autumn/winter peaks, a decline in spring and an increase in summer 1981. Magnesium levels in this soil were classified as high and occupied 12.9% in the A and 15.4% of C.E.C. in the A and B horizons respectively.

The amounts of soluble sodium in the A and B horizons were significantly correlated at the 95% confidence level and show an autumn/winter trough followed by increased concentrations in spring and early summer. Exchangeable sodium shows no obvious seasonal pattern in either horizon but a single large peak is evident in July 1981. For the A horizon levels are classified as low to moderate and only 1.4% and 2.9% for the A and B horizons of C.E.C. is occupied by sodium. More sodium is found in the soil solution and this reflects the weak bonding of sodium to the clay-humus complex.

Potassium is a major component of the sandstone and shales found in this area and is probably derived from the micaceous clay mineral, illite, which was identified in this soil. Potassium in the acid soil solution has little power for replacement of other cations and is therefore susceptible to leaching losses. Potassium is a macronutrient and is present in greater amounts than either nitrogen or phosphorus but the majority is held in the non-exchangeable form trapped in the clay mineral structures. However, gradual weathering replenishes the available potassium status. Soluble potassium shows a winter 1980 trough followed by an increase with a February 1981 maximum. A gradual fall to a July 1981 low is seen with both A and B horizons exhibiting a similar pattern. Exchangeable potassium exhibits a distinct winter 1980 trough followed by a rapid rise in concentration in spring 1981. Levels decline gradually to a June minimum and then rise to a peak in July. Potassium occupies 6.5 and 6.7% of C.E.C. for the A and B horizons respectively and this level is high in comparison with other soils (Curtis et al, 1976). Exchangeable ammonium levels are also comparatively high occupying 5.9% and 7.7% of the C.E.C. for the A and B horizons. A large isolated peak occurs in February 1981 and concentrations rise in the summer of 1981 as did soluble ammonium. A peak is also seen in July 1981.

The plot of specific conductance summarises the behaviour of most of the soluble ions in the soil solution and can be used as an approximate measure of the total dissolved solids (Foster et al, 1981). Autumn and winter peaks are evident with troughs occurring in March, April and May. The variation in the relative amounts of dissolved solids is a reflection of the dynamic nature of the soil solution in response to soil conditions.

iii) Field Soil Solutions

The extraction of a soil solution in the laboratory creates artificial conditions and does not provide a true indication of the soil solution in the field. A soil water extract measures the potential soluble ion concentrations which would be present if the soil were in a saturated state for a prolonged period. On the hillslope the composition of soil water is primarily dependent on the soil physical properties which determine soil water residence times and the matric suction of the soil. The records for vacuum lysimeter samples were not continuous due to instrument failure, vandalism and, during summer months, the matric suction of the soil exceeded the vacuum applied to the lysimeter pot thus preventing sample collection. Therefore, results are not plotted and the following description of solute concentrations is based on the general trends presented by the different lysimeters at 15 and 25cm. Acidity at both depths remained very constant between pH 3.9 and 4.0; minor changes over time were not detected due to the insensitivity of the analytical instrument used. Nitrite levels were negligible whilst ammonium concentrations were very low in the upper horizon but the mean value increased in the B horizon to 1.2mg l^{-1}. Phosphorus levels were extremely low but did vary, showing peaks in concentration at both depths for autumn 1980 and 1981 and a large peak in January 1981. Concentrations also rose in the summer months. Potassium and chloride showed a similar pattern to each other exhibiting summer and autumn peaks. Calcium and magnesium showed peak concentrations in January 1981 with a slight rise during summer. Nitrate levels remained fairly constant throughout. Sodium exhibited an exponential decay in concentration in all lysimeters

from the beginning of the experiment with values in one sampler decreasing from 61.0 to 5.0mg l^{-1}. This pattern suggested an initial contamination in the porous cup, plastic tubing or PVC piping, samples of which were soaked in deionised water and dilute hydrochloric acid for one week, but no significant increase in sodium concentrations was observed. The explanation for this pattern is therefore unknown.

The solutes in the A horizon soluble extracts were correlated with soil water from the vacuum lysimeters at 10cm and the B horizon extracts with soil water from 25cm depth. A total of only four significant correlations were found; calcium in the B horizon correlated with two lysimeters at 25cm depth whilst potassium in the A horizon correlated inversely with one lysimeter at 10cm depth and positively with another lysimeter at the same depth. Whilst no statistical validation of the comparability of solutes in the two extracts can be made, the underlying trends seem to be similar. The absence of significant correlations between the solutes in soil water extracts and lysimeter samples appears to confirm the criticisms of England (1974) who stated that 'one cannot be sure from what macroscopic volume of soil the sample was extracted nor from which pores it was drained'. Lysimeter samples may not, therefore, be representative of the soil water found in both macro and micropore situations. However, the sample may be more representative of the most mobile fraction of water in the soil matrix than the soluble extract.

Most solutes in soluble and lysimeter extracts possessed autumn/winter peaks with minor peaks during the summer months.

It is suggested that the autumn/winter peaks were attributable to the displacement of solute rich water which was held in the micropores and the mobilisation of evaporites.

The occurrence of throughflow was infrequent and the volumes which were collected were small. Consequently the importance of throughflow as a medium for solute transfer was negligible. The samples which were analysed showed that potassium, chloride and phosphorus were the most abundant ions. Throughflow, especially at the Ah horizon/litter interface moves rapidly and only the readily soluble elements will be taken up. No estimate of solute fluxes on the hillslope was made as the area contributing draining water to the throughflow pits was unknown. Foster (personal communication) showed that at site 1 throughflow occurred on a more regular basis, but the total contribution to streamflow was minimal.

5.4.0. Groundwater and Surface Water Chemistry

The chemical composition of groundwater and surface water is primarily dependent on the quality of water which derives from the soil profile and the nature of the soil and parent material in the saturated zone. All plotted values represent the mean weekly concentration for each biomass sampling period.

Figure 5.7 plots the mean weekly unweighted solute concentrations for each biomass sampling period (mg l^{-1}), for the groundwater sampled at borehole 1. Calcium, magnesium, sodium, nitrate and ammonium all increase in concentration with the falling water-table and show significant positive linear correlations with each other and the depth of the water-

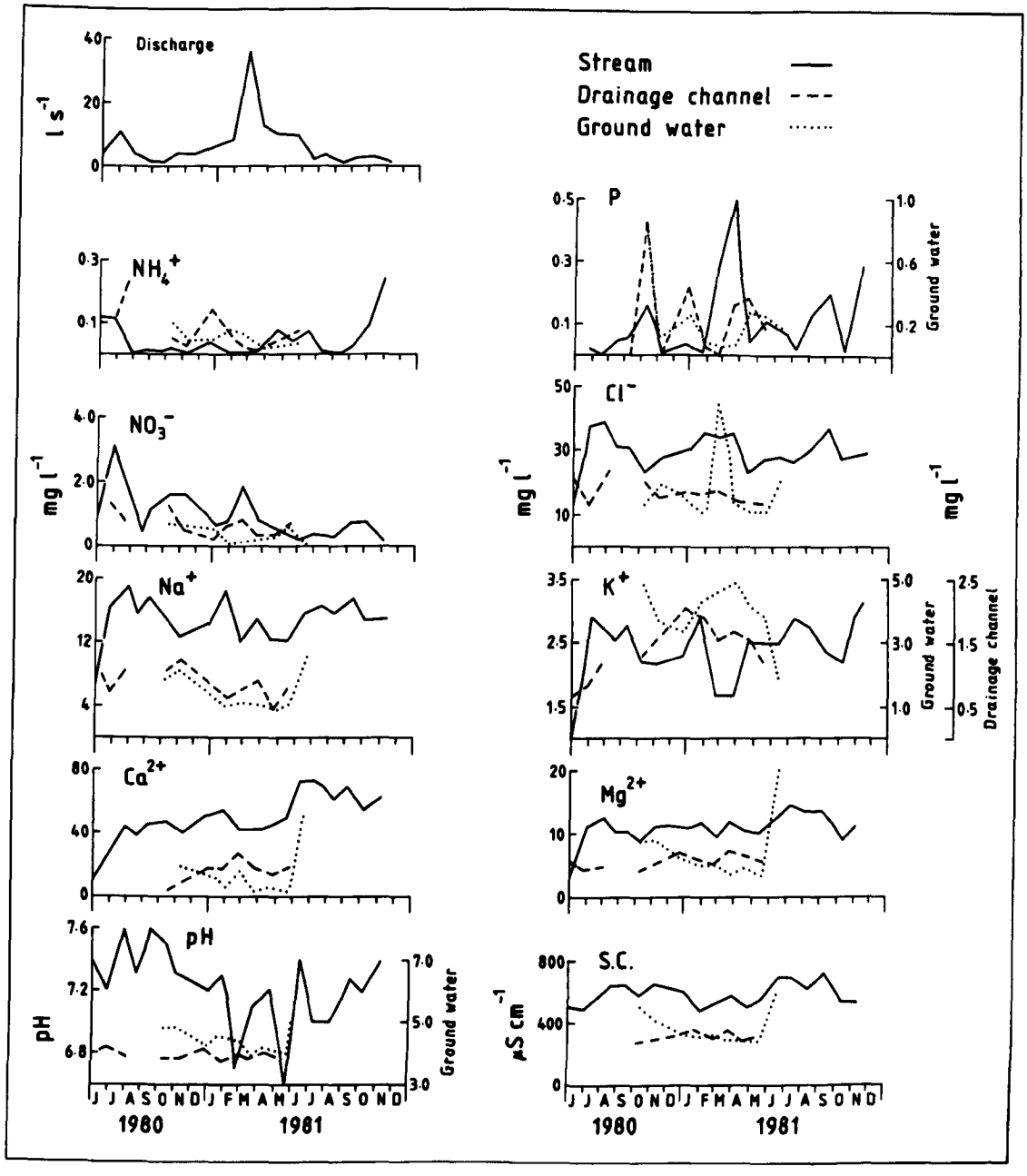


Figure 5.7 Stream, ground water and drainage channel chemistry

table from the soil surface (Table 5.14). Specific conductance and pH also exhibit positive relationships with the depth of the water-table. Potassium is the only ion which increased in concentration with the rising water-table and shows a negative correlation with the depth of the water-table. The matrix in Table 5.14 shows all cations are significantly intercorrelated whilst only two significant relationships are observed between the anions and any other variable. The absence of significant correlations suggests that other ions such as sulphate or bicarbonate form soluble compounds with the cations within the groundwater. Data from site 1 shows there to be significant quantities of these anions in the groundwater. Chloride concentration exhibits a peak in March 1981 which coincided with a large rainfall input though no corresponding increase in sodium is seen despite a significant positive correlation between the two elements in precipitation and groundwater. Table 5.15 describes the characteristics of the measured variables. The percentage variance of the ions is fairly high due to the diluting and distillating effect of the changing water level. The maximum weekly concentrations of calcium and magnesium were 85% higher than their mean values and were detected in June 1981 when the perched water-table was falling. This effect was probably due to the concentrating effect of the falling water-table by evaporation losses on solute levels. Potassium is a highly labile monovalent ion which is readily soluble and as the water-table rose potassium in the previously unsaturated zone may have been dissolved, thus increasing its concentration in the groundwater. When the water-table fell potassium would be preferentially taken up by the soil as a consequence of the ratio law (Russell, 1961) displacing divalent ions such as calcium and magnesium.

Table 5.14 **Cross correlation matrix for variables in the groundwater**

	Ca	Mg	Na	K	NH_4	NO_3	NO_2	Cl	P	SC	pH	depth
Ca												
Mg	+											
Na	+	+										
K	-	-	-									
NH_4	+	+	+	-								
NO_3												
NO_2												
Cl			+									
P												
SC	+	+	+	-	-							
pH	+	+	+	-	-					+		
depth	+	+	+	-	-					+	+	

+ significant positive correlations

- significant negative correlation

Sample size = 30

Confidence level = 95%

Table 5.15 **Groundwater and Drainage Channel Characteristics**

	Ca	Mg	Na	K	NH_4	NO_3	NO_2	Cl	P	SC	pH	depth
										uS cm^{-1}		cm
Groundwater characteristics (mg l^{-1} wk^{-1})												
$\bar{x}$	13.7	7.2	5.6	3.8	0.06	0.3	0.14	16.8	0.017	369.1	4.5	105.6
%CV	133.5	111.4	48.7	38.9	121.0	107.6	554.0	104.3	192.9	35.9	21.0	28.1
SE	3.1	1.4	0.5	0.2	0.01	.05	0.13	3.0	0.006	22.4	0.16	5.0
min	0.5	2.1	0.4	1.0	0.0	0.0	0.0	8.2	0.0	275.0	3.8	65.0
max	71.9	48.0	11.5	6.9	0.33	1.1	4.5	110.9	0.15	768.0	7.2	210.0

Sample size = 30

Drainage channel characteristics (mg l^{-1} wk^{-1})												
$\bar{x}$	5.7	5.9	6.8	1.5	1.2	2.1	0.04	16.0	0.012	306.3	3.9	
%CV	67.1	19.9	31.1	46.6	491.1	391.7	413.6	30.4	184.7	13.8	7.0	
SE	0.7	0.2	0.4	0.1	1.1	1.5	0.03	0.9	4.0	7.7	0.051	
min	1.2	4.2	0.9	0.6	0.0	0.0	0.0	8.8	0.0	220.0	3.5	
max	18.9	7.9	10.4	3.4	31.5	44.4	1.0	33.4	0.086	437.0	4.9	

Sample size = 27

Figure 5.7 also plots the unweighted solute concentrations for water sampled from the drainage channel. Calcium concentrations increased in winter from low summer values and the peak value coincides with the peak stream discharge in March. Sodium and chloride levels show similar characteristics to each other decreasing in concentration in the winter months. Potassium illustrates higher concentrations in January, decreasing through the spring months, ammonium also exhibits a similar pattern. Nitrate concentrations decrease during the winter but show a small peak when stream flow is at maximum in March 1981. Phosphate levels are variable but are negligible in October of both years. Magnesium, pH and specific conductance all show a similar pattern with little change throughout the year. There were few significant correlations between elements within the drainage channel, but it was noticeable that highly significant relationships occurred between ammonium, nitrate and phosphate. These three ions also showed high percentage variation with their maximum concentrations occurring on 22nd October 1980 when the first flow of the autumn was recorded (Figure 5.7). The variance of conductivity and pH is very low despite the wide range of flow conditions which were observed.

The discharge weighted solute concentrations for the streamwater are presented in Figure 5.7, this method of plotting eliminates the seasonal effect of varying flow conditions and highlights any changes in ion concentrations not attributable to dilution and evaporation. The graphs show that concentrations do not exhibit the marked seasonal trends already recorded on the hillslope (Foster et al, In Press). In general the ions exhibit very little variance in concentration with the exception of nitrate and phosphate, despite the greater % variation in stream discharge. Table 5.16 gives the % CV for each variable monitored in stream water.

Table 5.16 **Stream water characteristics**

	Ca	Mg	Na	K	NO_3	Cl	NH_4	NO_2	P	pH	SC	Disch $l\ sec^{-1}$
$\bar{x}$	54.7	11.0	16.0	2.3	1.01	32.3	0.03	0.05	0.07	7.37	608.9	6.21
%CV	28.5	27.7	26.4	23.0	78.8	39.3	51.9	21.2	160.0	4.9	16.6	189.1
SE	1.75	0.34	0.48	0.06	0.09	1.43	0.8	0.5	0.013	0.041	11.4	1.32
min	22.9	4.3	8.1	0.9	0.0	15.1	0.0	0.0	0.0	6.35	332.4	0.25
max	89.7	30.5	37.4	3.7	5.2	123.1	0.15	0.1	0.48	8.3	910.0	88.27

Sample size = 79

Values are not discharge weighted and represent mg l^{-1} wk^{-1}

Likens et al (1977) found that volume weighted concentrations of ions in stream water were far less variable than in precipitation but they did observe a seasonal decrease in nitrate and potassium levels when plant activity utilises these elements. Figure 5.7 does show decreased nitrate and potassium concentrations in spring/summer 1981 but no obvious seasonal trend is apparent. Several ions show troughs which correspond with peak discharge, such as calcium, sodium and potassium, whilst nitrate, ammonium, hydrogen and phosphate all increase in concentration for the same period. Phosphate, chloride, acidity and potassium show a general increase in the autumn months, whilst only calcium and ammonium show increases corresponding to the frass fall period. It is noticeable that the acidity of the stream is at its lowest during June 1981. Table 5.17 illustrates the significant linear correlations which exist between unweighted ions and with discharge. Several significant relationships are apparent, for example, calcium, sodium, potassium, specific conductance and pH have negative correlations with discharge. This relationship indicates that an increased flow dilutes the concentration of these ions, though the relationship is not so simple in the short term. Walling and Foster (1975) showed that during a storm event calcium, sodium and magnesium all exhibited dilution, but then increased in concentration followed by a subsequent fall in concentration. They attributed this effect to the 'flushing' effect which displaces solute rich soil water from the finer pores of the soil matrix. In a second streamflow rise, the flushing effect was absent because solute rich water in the fine pore had been displaced. Nitrate and potassium have far more variable responses to discharge. Walling and Foster (1975) state that nitrate levels demonstrate a complex behaviour and Table 5.17 shows no significant correlation with discharge. Foster and Grieve (1981) state that the prediction of nitrate levels using a rating equation is difficult due to the

Table 5.17 **Cross correlation matrix for unweighted stream water variables**

	Ca	Mg	Na	K	NH_4	NO_3	NO_2	Cl	P	SC	Disch	pH
Ca												
Mg												
Na												
K	+	+										
NH_4												
NO_3	-	-		-	+							
NO_2		+				+						
Cl			+									
P					+							
SC	+		+					+				
Disch	-		-	-	+					-		
pH			+		-					+	-	

+ significant positive relationship

- significant negative reationship

Sample size = 65

Confidence level = 95%

variability of its response. Potassium does show an inverse relationship with discharge though Walling and Foster (1975) and Likens et al (1977) suggest the overall relationship is controlled by flushing, biologic activity and the frequency of storm events. Sodium and chloride exhibit a positive significant relationship and this may be indicative of the original precipitation source or their similar behaviour in the ecosystem.

The explanation of stream water chemistry is far more complex than any other parameter monitored, as concentrations depend on antecedent soil moisture conditions and the pathways which moving water has taken within the basin. A more detailed discussion of stream water chemistry is provided in Chapter 6 as concentrations reflect the processes and interactions in operation within the drainage basin.

5.5.0. Conclusion

Figure 5.8 shows the pathways which solutes may follow within the ecosystem and also the associated nutrient stores. Bulk precipitation and throughfall represent the inputs to the system. The diagram identifies an accumulation of nutrients in the vegetation biomass and also a soil and groundwater store of ions. Solutes were lost from the ecosystem in streamflow. Table 5.18 summarises the annual inputs and stores of nutrients from January to December 1980. The precipitation and frass inputs represent annual inputs kg ha^{-1} yr^{-1}. The quantities of nutrients in the oak leaves, twigs and bracken fronds are the maximum accumulations (kg ha^{-1}) and thus represent uptake from the soil. The values for bracken rhizomes and litter are the mean accumulations (kg ha^{-1}) for 1980. The quantity of water soluble and exchangeable ions in the soil was calculated using the mean annual concentration, bulk density of each horizon and assuming an average soil depth of 0.75m over the entire

Figure 5.8 **Nutrient Pathways and Stores**

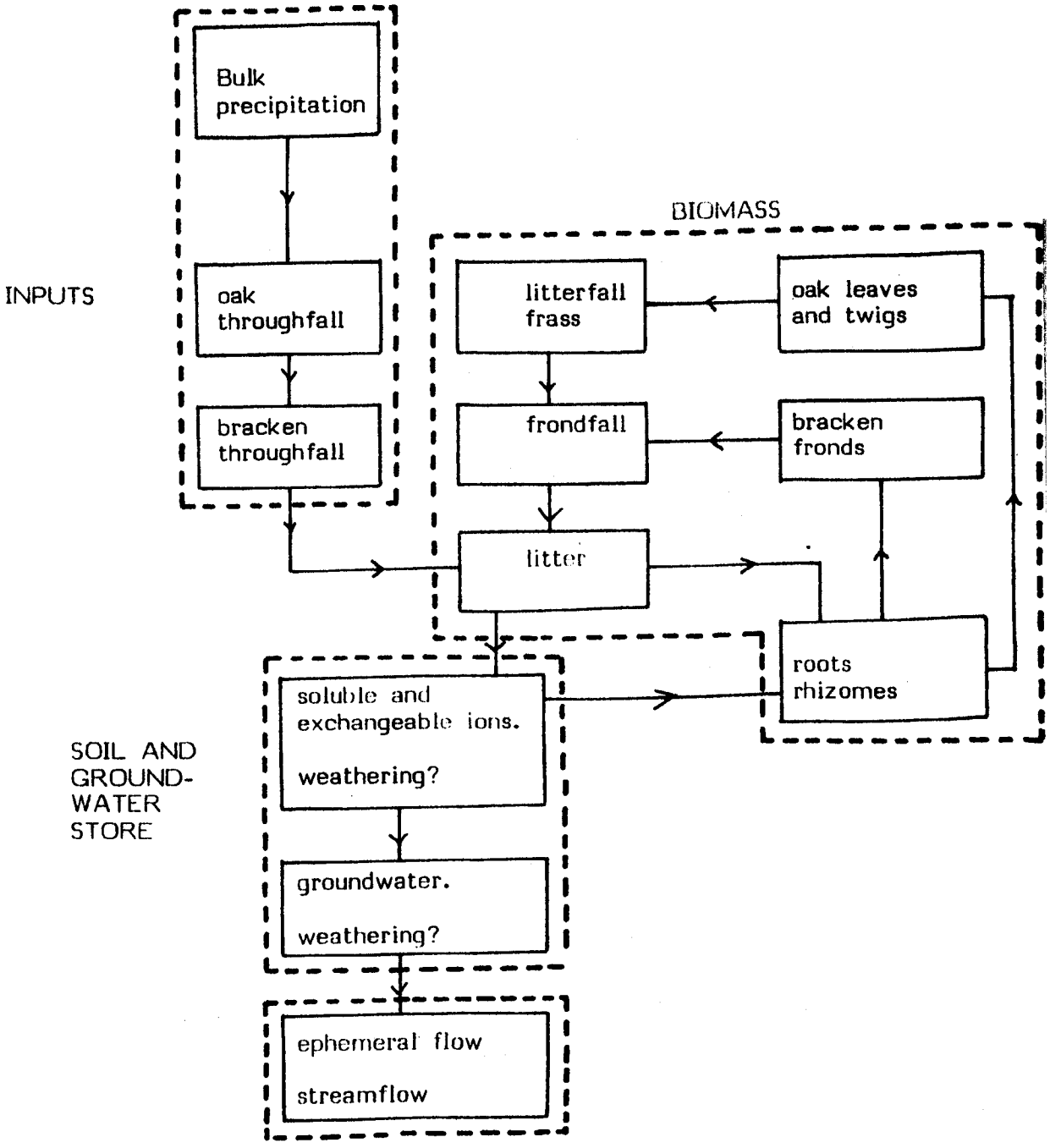


Table 5.18 **Nutrient fluxes and stores for 1980 (January-December) kg ha^{-1} yr^{-1}**

	Ca	Mg	Na	K	N	Cl	P
Bulk precipitation	15.1	4.9	20.0	10.5	27.7	59.0	0.2
Oak throughfall	6.3	3.4	1.6	63.1	3.8	7.9	2.8
Bracken throughfall	0.0	0.6	3.1	21.9	-2.6	26.5	-0.3
Oak leaves and twigs	20.5	4.2	6.7	4.6	180.3	0.3	13.1
Oak litterfall	10.3	3.1	7.5	32.0	121.1	4.5	10.2
Frass	1.2	1.3	4.0	13.0	91.3	0.3	4.4
Bracken fronds	6.8	2.9	2.1	54.1	54.8	1.3	12.3
Bracken rhizomes	2.6	2.7	7.5	46.0	71.4	2.4	5.7
Frondfall	6.8	1.9	1.7	30.0	30.4	1.3	2.7
Litter	83.0	23.5	58.3	204.1	792.3	28.6	70.6
Soil water (extracts)	5143	782	1503	309	145	2015	152
Exchangeable cations	2216	3480	580	2584	210	-	-
Groundwater $\bar{x}$ mg l^{-1}	13.7	7.2	5.6	3.8	0.5	16.8	0.017
Ephemeral Drainage $\bar{x}$ mg l^{-1}	5.7	5.9	6.8	1.5	3.34	16.0	0.012
Weathering	102.4	20.4	12.7	?	?	4.7	-0.02
Stream	117.5	25.3	32.7	5.2	2.1	63.7	0.22
Annual loss/gain	-102.4	-20.4	-12.7	+5.3	+25.6	-4.7	-0.02

drainage basin. Values quoted are kg ha^{-1} for A and B horizons. No calculation of the groundwater and ephemeral drainage stores was possible and the values in Table 5.18 therefore represent the mean weekly values in mg l^{-1}.

Stream losses are kg ha^{-1} yr^{-1} and it can be seen that only potassium and total nitrogen, major plant nutrients, represent net gains to the drainage basin. Phosphorus is therefore likely to be the limiting nutrient in plant growth. Foster and Grieve (1981) showed that hydrogen was also a net gain during 1978-80 in this ecosystem, emphasising the importance of soil acidity and leaching. Cation losses in stream water were dominated by calcium and data from site 1 showed bicarbonate to be the major anion loss. Foster and Grieve (1981) attribute the excess of ions in stream water over precipitation inputs to solute release by weathering in the soil and groundwater. Calcium is probably derived from the calcareous bedrock and accounts for the high losses. Table 5.18 illustrates that large quantities of nutrients are held in the soil and litter stores, but no calculation of the nutrients stored in total oak biomass has been attempted. These stores may have an important effect on the regulation of ion concentrations in the ecosystem. With the exception of calcium and magnesium, the net loss of other solutes is comparatively small, suggesting a fairly stable ecosystem.

Chapter 6.0 ECOSYSTEM INTERACTION: TOWARDS AN EXPLANATION OF SOLUTE CONCENTRATIONS IN A FORESTED ECOSYSTEM

6.0.0. Introduction

The interaction between the biotic and abiotic components of the ecosystem was investigated using several statistical methods which sought to identify simple and complex relationships between the variables monitored within the drainage basin. No known comparable work exists in the literature and the following analysis is probably one of the first attempts to derive a statistical model describing the relationships between solute concentrations within a forested ecosystem.

A data matrix, for each of the elements monitored, containing 42 variables and 19 observations was established. Each observation represented weekly means for each vegetation sampling period. It was not possible to calculate monthly totals or means since the vegetation sampling period was not constant. Table 6.1 gives the 42 variables which were incorporated into each data matrix. The first column shows the range of monitored environmental variables which describe temperatures, water volumes and biomass. These data comprised an independent variable data set for each element monitored. The second, third and fourth groups of variables contain water, soil and vegetation parameters respectively and represent the measured nutrient concentrations. Nitrate, nitrite and ammonium were independently determined for the soil and water samples and their values were summed to give total nitrogen for incorporation in the data matrices.

Table 6.1 **Variables in the data matrix, variable codes and variable abbreviations**

ENVIRONMENTAL VARIABLES

code		
1	maximum air temperature)	air
2	minimum air temperature)	temperature
3	soil temperature	
4	rainfall volume	
5	monthly A.P.I. (M.API)	
6	effective rainfall	
7	soil moisture deficit	
8	potential evapotranspiration (PE)	
9	stream discharge	
10	frond biomass	
11	rhizome biomass	

CHEMISTRY

code	**water variables**	**abbreviation**
12	rainfall	rain
13	oak throughfall	otfall
14	bracken throughfall	btfall
15	groundwater	GW
16	ephemeral drainage	DC
17	stream water	stream
	soil variables	
18	A horizon exchangeable	AE
19	A horizon soluble	AS
20	B horizon exchangeable	BE
21	B horizon soluble	BS
22	lysimeters 10cm	lysim 10
23	25cm	lysim 25
	50cm	lysim 50
	throughflow pit 3A	T3A
	3B	T3B
	4A	T4A
	4B	T4B
	vegetation variables	
24	bracken fronds	frond
25	bracken rhizomes	rhizome
26	oak leaves/twigs	oak
27	oak litterfall	litterfall
28	litter	litter

However, an immediate criticism can be directed at the organisation of each data matrix. The water and soil variables were monitored on a weekly or fortnightly basis and thus the calculation of weekly means for each biomass sampling period led to decreased sensitivity of the original data. Whilst the weekly means did incorporate any extreme event such as frassfall, the true extent of the impact on other variables would have been partially hidden by the use of a mean value.

Analysis of the data was achieved by first producing a cross correlation matrix using simple linear regression analysis. Multivariate statistics were then employed to identify the relationship between each dependent nutrient concentration and a number of independent variables. This was performed using stepwise multiple regression. The final analysis attempted to identify groups of inter-correlated variables using the principal component technique. The following sections describe the use of these techniques and present the results of the statistical analyses.

6.1.0. **Bivariate correlation and regression analysis**

The first step in the analysis of all variables was the derivation of a cross correlation matrix for each element. This was obtained by simple linear regression analysis using a Statistical Packages for Social Scientists (SPSS) programme, (Nie et al, 1970). The aim of the regression was to measure the strength and direction of a relationship between two variables (Ebdon, 1978). In this study the relationship can also be interpreted as a measure of the dependence of the nutrient concentration of one variable on another variable concentration or an environmental parameter. Certain relationships have already been discussed, for example, precipitation with throughfall, but this section investigates correlations which may occur

between any variable on the hillslope and stream solute concentrations in an attempt to identify simple direct relationships. Graph plots of these relationships were initially obtained using the SPSS Scattergram routine which provided a means of determining the type of regression analysis that should be used.

The technique of linear regression is frequently misused, as the independent variable should not be a sample measurement (Ebdon, 1978) since errors will be expressed along both axes of the regression. Cross correlation using sample measurements was unavoidable in this study and therefore Ebdon (1978) stated that the technique is only justified if there is a negligible amount of measuring error encountered with the independent variable. Previous chapters have discussed analytical, sampling and spatial variability and in some cases the criticism was justified. However, the cross correlation did provide a means of identifying direct relationships between variables in the matrix despite the loss of accurate predictive data. The use of a technique such as reduced major axis to remove the residual errors of both variables was not necessary. The correlation matrix for each nutrient analysed provided a total of 798 coefficients; the significant correlations are therefore described using four main groups of relationships, first, the correlations between precipitation input and soil nutrient concentrations, secondly, soil and vegetation relationships and thirdly the soil and water correlations. The final group of correlations describes all the relationships between environmental variables and the remaining vegetation, soil and water chemistry parameters.

The woodland floor receives a combination of rainfall and throughfall depending on vegetation cover. Solute loadings of gross and net precipitation were therefore correlated with the soil exchangeable and

soluble ion concentrations. The solute levels in gross precipitation and oak throughfall did not significantly correlate with any soil nutrient, in either the exchangeable or the soluble form. Bracken throughfall only significantly correlated with the B horizon soluble level of chloride. Precipitation must pass through the litter layer before it reaches the soil horizons and some modification of precipitation chemistry will have taken place. Correlation of precipitation with litter chemistry shows that only potassium in rainfall has a significant relationship with litter levels.

The absence of many significant relationships indicated that water chemistry was radically altered within the soil and litter layers and other factors must be responsible for the chemical composition of soil water and the level of exchangeable cations. Chapter 5 has already shown that there were few significant relationships of soil nutrient concentrations with soil moisture and soil organic carbon content. The present analysis only identified significant correlations of precipitation volume with soluble sodium levels in the A horizon and soluble chloride in the B horizon. Both these substances are relatively unimportant for biological growth (Russell, 1961) and their presence may relate to the oceanic derived quantities in precipitation moving through the soil matrix. All other nutrients monitored are considered to be macro or micro plant nutrients (Black, 1968) and their concentrations in the soil were probably influenced by plant uptake and release. The soil is a highly complex system and whilst it relies on precipitation for nutrient inputs and water its complexity masks any direct relationships which may occur.

Exchangeable and soluble ion concentrations in the soils obtained during vegetation sampling and the soils from the constant source sampling area were correlated with all nutrient concentrations in bracken fronds,

rhizomes, oak leaves and twigs, litterfall and the litter layer. The significant relationships are given in Table 6.2A.

Calcium levels in litter are correlated with exchangeable calcium in the A and B horizons. Exchangeable ammonium in the A horizon correlates with total nitrogen in the litter. Soluble chloride and exchangeable sodium in the B horizon exhibit significant relationships with the litter concentrations. The decomposition of litter in this woodland was a gradual process with nurients being selectively released over time depending on their physiological function and the nature of the dead vegetation, for example, it has been shown that potassium, sodium and chloride are leached very quickly from fresh litter but calcium, phosphorus and nitrogen accumulated in the litter after abscission. The relationship was further complicated because litter was composed of a variety of vegetation fractions at different stages of decomposition, as well as other important fractions such as frass. Soil nutrient concentrations are partially reliant on precipitation inputs which pass through the litter and also the rate and nature of decomposition. Several direct correlations of nutrient concentrations were therefore expected. The occurrence of positive significant correlations between litter and B horizon sodium and chloride concentrations indicates the similar behaviour of both ions and suggests their relative biological inertness. Exchangeable calcium and ammonium in comparison to sodium and chloride are more tightly bound to the soil exchange sites, whilst litter absorbs calcium and nitrogen from the surrounding water. Inputs of calcium and nitrogen to the forest floor may be preferentially stored by the soil and litter. Soluble magnesium in both soil horizons exhibits an inverse relationship with bracken frond concentrations whilst soluble and exchangeable nitrogen in the A horizon are positively correlated with frond concentrations. Uptake of nutrients

Table 6.2A **Significant linear relationships between soil and vegetation chemistry**

	Ca	Mg	Na	K	N	Cl	P
A horizon							
Exch	litter				frond litter oak		
Sol		frond		litterfall	frond		
B horizon							
Exch	litter		litter	litterfall			
Sol		frond				rhizome litter	

Table 6.2B **Significant linear relationships between soil and selected water chemistry variables**

	Ca	Mg	Na	K	N	Cl	P
A horizon							
Exch					T4A		
Sol			stream		T3A T3B		DC
		DC			T4A		
B horizon							
Exch		$\overline{GW}$ $\underline{DC}$		DC			
Sol		GW DC					$\overline{DC}$ T3A

GW indicates a significant positive correlation

$\overline{GW}$ indicates a significant negative correlation

$\underline{GW}$ correlation with soils from the constant source area.

confidence level = 95%

by the growing bracken from the soil would result in an inverse correlation as shown by magnesium, however, the negative relationship may also be explained by other processes, for example, the autumn/winter peaks in soil magnesium levels may be due to weathering release as the soil becomes wetter and not to the diminished plant uptake. Potassium in litterfall is significantly related to soluble levels in the A horizon and exchangeable levels in the B horizon. An inverse relationship would probably have been expected here, as potassium is readily leached from leaves and fronds before abscission and frondfall respectively. The positive relationship which arises may result from the immediate leaching of nutrient rich litter fractions; the correlation results from the fresh litter input and the newly enriched soil concentrations. Rhizome concentrations in the soil are only correlated with chloride levels in the B horizon. This relationship may reflect an osmotic balance between the soil solution and rhizome uptake of this element.

The evidence shows that soil nutrient concentrations are related to certain vegetation inputs and uptake but no consistent relationships and trends are apparent from a simple bivariate analysis.

Water passes through the soil by percolation or lateral flow to enter the groundwater and eventually the stream. Therefore soil exchangeable and soluble ions were correlated with solute concentrations in throughflow, groundwater, the drainage channel and also in stream water. Table 6.2B shows that soluble magnesium and phosphorus are significantly correlated with solute concentrations in the drainage channel whilst nitrogen in throughflow from the A and B horizons correlates with soluble nitrogen in the A horizon. Magnesium in the exchangeable and soluble forms correlates with the groundwater concentrations but the former correlation

is inverse. Soluble sodium in the A horizon is the only ion to significantly correlate with the discharge weighted concentrations of the stream.

Burt (1979) studied the variation in solute concentrations of soil and stream water during throughflow events. He was able to show that during a storm event the throughflow concentrations of ions remained relatively constant compared with the dilute concentrations in the stream during peak runoff. Subsequent 'flushings' of throughflow increased the solute concentration of the stream. In this catchment the contribution of throughflow to runoff was negligible and stream water concentrations were more likely to be related to the concentrations of solutes in the drainage channel or groundwater. Table 6.3 reveals the significant correlations associated with streamwater concentrations and it can be seen that no relationships exist between the stream and groundwater or the ephemeral channel. Sodium in the stream correlates with a range of variables all of which have distinctive seasonal patterns. The origin of sodium in this catchment is mainly from precipitation and several significant relationships have already been identified in relation to its input and transfer through the system. The relationships of other nutrients with the variables in Table 6.3 is less obvious though calcium, phosphorus and nitrogen stream concentrations are all inversely related to the monthly A.P.I. As the A.P.I. increases, the soil becomes wetter and runoff to the stream increases. Solute concentrations may therefore be directly diluted in the case of nitrogen and phosphorus, or calcium may be taken up by the soil as a consequence of the ratio law (Russell, 1961). Likens et al (1977) showed that nitrogen and potassium in stream water decrease in summer due to plant uptake. No evidence for this relationship was observed, but calcium in stream water was inversely related to bracken rhizome and

Table 6.3 **Significant linear relationships between volume weighted stream chemistry and all other variables**

Ca	Mg	Na	K	N	Cl	P
$\overline{M}$.API	lysim 10	frond biomass	rainfall vol.	$\overline{M}$.API	$\overline{b}$tfall	$\overline{M}$.API
$\overline{r}$hizome		air temp.		rain		oak
$\overline{l}$itter		$\overline{d}$ischarge		lysim 25		lysim 10
		SMD				
		frond				
		AS				

abbreviations are listed in Table 6.1
$\overline{M}$.API significant negative correlation
M.API significant positive correlation
confidence level = 95%

litter concentrations. Exchangeable and soluble magnesium in the B horizon significantly correlate with groundwater concentrations though the former relationship is inverse. This relationship was described in Chapter 5 and is associated with the ratio of soluble and exchangeable ions in the soil (Russell, 1961).

The plots of the environmental parameters monitored, against time, exhibited obvious seasonal characteristics, with the exception of the monthly A.P.I., effective rainfall and rhizome biomass. Harmonic analysis was employed to identify statistically significant seasonal trends in the data by correlating environmental parameters and the nutrient concentrations of all other variables monitored with time. This analysis was performed using the Biomedical Data (B.M.D.) package, periodic regression and harmonic analysis (Dixon, 1977). The technique fitted two complete sine curves to the data and output a table of observed and predicted values and their residuals. No correlation coefficient was produced by this programme and therefore the output tables were subjected to simple linear regression using the Minitab data package (Ryan et al, 1981).

The environmental variables of temperature, S.M.D., P.E., discharge and frond biomass exhibited correlation coefficients which were significant at the 98% level. However, it was found that the technique was not suitable for the identification of seasonal trend in the nutrient concentration of the soil, water and vegetation samples. The nutrient plots presented in Chapter 5 showed peaks in concentration throughout the study period which were not only associated with sampling and analytical variability but also the changes which were instigated by isolated events. Examples of these peaks include the contamination of throughfall by frass,

litterfall inputs of budscales with other nutrient rich fractions and the storm event which contributed branches to litterfall. This type of event occurred throughout the study period and introduced concentrations of nutrients which, on occasion, were greater than the autumnal peaks which were identified. Bliss (1958) recommends the smoothing of the data using moving averages and this was done by Foster and Grieve (personal communication) for carbon concentrations in the soil in this catchment using a three point running mean. Whilst significant annual harmonics were found for one year, the random and spatial variability of the data obscured the statistical significance of the results. No attempt was made to smooth the data for this study. The absence of significant annual harmonics was due to the additional, mid-season inputs and fluxes. As this technique was employed simply as a descriptive statistic, no further attempt was made to characterise the data using polynomial regression. For example, Gregory (1978) states that trends may be highly complex and harmonics can overlap each other and therefore more sophisticated techniques of analysis would be required to characterise this type of trend.

Simple linear regression analysis was performed between the environmental variables and the nutrient concentrations of water, soil and vegetation samples. Temperature, potential evapotranspiration and frond biomass all revealed similar correlations with dependent variables and this was due to the highly significant intercorrelations which resulted between these environmental parameters. The significant correlations which do occur with the intercorrelated variables represent the nutrients which exhibit a seasonal trend in their concentrations. For example, the magnesium, potassium, nitrogen and phosphorus concentrations of bracken fronds all significantly correlate with air temperature, soil temperature and frond biomass (Table 6.4). The environmental variables, S.M.D., effective

Table 6.4 **Relationships between environmental and solute parameters in the hillslope system**

	Air Temp	Soil Temp	PE	SMD	Rainfall vol	Monthly API	Effective Rainfall	Frond Biomass	Rhizome Biomass
Ca	oak -rainfall -DC	oak -rainfall -DC	-rainfall -DC T3B T4A	oak -rainfall rhizome XAS T4A	-DC -groundwater	lysim 10 litter	rainfall	rhizomes oak -XAS groundwater	lysim 10
Mg	frond XBE AS BS	frond XBE AS BS DC T3A	bracken tfall XBE				groundwater	frond rhizome oak AS BS DC	frond DC BS
Na	-rainfall -lysim 50	-rainfall -AE -lysim 50	-rainfall -oak tfall	frond groundwater T4A lysim 50 lysim 25	oak XAS BE T3A		rainfall oak tfall	frond groundwater -lysim 50 -lysim 10	frond lysim 10
K	frond oak oak tfall -DC T3A T4A	frond rhizome oak DC T3A T4A lysim 25	oak oak tfall DC XBE T3A T4A	frond rhizome T4A lysim 25	groundwater	rhizome	groundwater T3A lysim 10	frond lysim 30	frond rhizome lysim 10

Continued..

Table 6.4 Continued

N	frond oak XAE AS BE	frond oak T4A	oak AE	frond litter XAE	litter		litterfall oak	frond litter XAE	frond XAS
Cl	T3A T4A	frond oak T3A T4A	-oak tfall -litter AS BS T3A T4A	frond oak T4A	oak tfall -XBS	-oak -bracken tfall -DC -lysim 25	oak tfall -T4A	frond oak T4A	frond rhizome -XAS
P	frond oak T3A T3B lysim 25	frond oak lysim 25	T3A T3B lysim 25	lysim 10		rainfall	-T3B	lysim 25	lysim 10 lysim 25

lysim 50 soil solution at 50cm

abbreviations are listed in Table 6.1

-litter significant negative correlation
litter significant positive correlation

Confidence level = 95%

rainfall and the monthly A.P.I. are all different measures of the amount of moisture in the soil but it can be seen in Table 6.4 that they do not correlate with similar nutrient variables. It is clear from Table 6.4 that no overall pattern of correlations exists, despite the many significant relationships which do occur.

The results of the bivariate linear regression analysis emphasise that whilst some direct relationships were identified and their occurrence is easily interpreted, there are many relationsips for which there is no direct explanation. Similarly some variables did not significantly correlate with any other parameter and the final solute pathway, the stream, exhibited only one significant correlation in the entire analysis. Clearly the technique of linear regression was inadequate for the explanation of solute pathways and a more complex multivariate approach was required.

6.1.1. **Multivariate Analysis**

Multiple regression analysis is a technique which can describe and predict the relationship between a dependent variable and a set of independent variables. The technique assumes a normal distribution of the data and minimal collinearity in the data set. Nie et al (1970) state that the technique should not be used when extreme collinearity exists - that is correlation coefficients of greater than 0.8 are unacceptable. Multiple regression was used in this experiment to identify the variables which had causal effects on the properties of a dependent variable. This was performed using the SPSS stepwise regression package (Nie et al, 1970). This method introduces independent variables into an equation one by one and determines which variables are statistically significant in explaining the variance of the dependent variable. The order of variable entry is

decided by initially using the independent variable with the highest zero order correlation; the effect of this variable is then removed and the method then takes the next highest partial correlation coefficient. This process continues until the inclusion of further variables does not significantly explain any of the variance of the dependent variable, thus removing unnecessary variables from the equation. A major problem which was encountered when using this technique was the unstable effect that highly intercorrelated variables had on the regresssion constants. This collinearity effect was seen when the most significant of the intercorrelated variables was incorporated in the regression equation and thus explained the majority of the variance in the dependent variable, which may have also been partially accounted for by the other collinear variables.

The highly intercorrelated variables were the environmental parameters of soil temperature, maximum and minimum air temperature and potential evapotranspiration. It was therefore decided to eliminate all but one of these variables, namely soil temperature, prior to the analysis. This approach was thought to be justified since soil temperature is a direct function of air temperature (Mather, 1974) and the calculation of potential evapotranspiration was based on values of air temperature. Table 6.5 gives the correlation coefficients of these variables with soil temperature.

Table 6.5 **Correlation coefficients of intercorrelated environmental variables**

	Max. temp	Min. temp	P.E.	Frond Biomass
Soil temp.	.96915	.97109	.76441	.78545

All coefficients are significant at the 99.9% level

Sample number = 19

Table 6.5 shows that frond biomass was also highly correlated with soil temperature, but this variable was not removed from the calculations since it was below the value of 0.8 recommended by Nie et al (1970) for exclusion.

The bivariate analysis failed to identify many significant relationships of vegetation and precipitation chemistry with soil and soil water chemistry. Multiple regression analysis was employed to identify any groups of vegetation and precipitation parameters which together would explain a large amount of the variance in the exchangeable cation content of the soil and soil water solute concentrations.

Table 6.6 gives the significant independent precipitation and vegetation variables which partially explain the variance in soil exchangeable and water soluble ion concentrations during the study period. The maximum percentage of explained variance occurs for soluble phosphorus in the A and B soil horizons. Bracken throughfall explained 61% and 72% for the A and B horizon concentrations respectively. The growth of oak leaves and twigs and the subsequent litterfall explain a further 11% of the variance in the A horizon, whilst bracken rhizome concentrations in the B horizon explain a further 2% of the variance. The maintenance of plant available phosphorus levels by weathering in this soil is unlikely as hydroxyl ions of iron, aluminium and manganese possibly precipitate the phosphorus before plants are able to take it up. The weathering of minerals in the soil is more likely to occur in the fine micropores where solid-solvent contact is prolonged and precipitation of phosphorus probably occurs. The solute rich water in these micropores is less available to plants as it is held in pore spaces at tensions greater than 2 bar. Therefore plant available phosphorus was presumably located in the larger pores of the soil

Table 6.6 **A multivariate explanation of soil nutrient concentrations**

	Ca		Mg		Na		K		N		Cl	P	
AE	litter	38	-		-		btfall	35	oak	32	-	-	
	brack	51					brack	50					
	rain	60					oak	55					
AS	-		brack	28	-		btfall	27	brack	25	-	btfall	61
			oak	48			oak	41				oak	70
			lfall	51								lfall	72
BE	-		-		btfall	25	-		-		-	-	
BS	oak	23	brack	34	-		-		oak	20	-	btfall	72
	brack	37	oak	72								rhiz	74

Abbreviations are listed in Table 6.1

Figures refer to cumulative percentage explanation of the dependent variable.

Sample size = 19; significance level = 95%

and represented the direct inputs of throughfall and percolating water. Similarly 55 and 41% of the A horizon potassium exchangeable and soluble ion concentrations respectively were explained by bracken fronds, bracken throughfall and oak leaf and twig concentrations. Potassium is readily leached from the soil horizons and the correlation with the top soil emphasises the importance of the exchange capacity of the organic matter in retaining potassium.

Chloride levels in the soil are not significantly explained by any of the independent variables. This finding was surprising as a large amount of chloride was supplied by precipitation and vegetation leachates. Likewise, only 25% of the variation in B horizon exchangeable sodium concentrations was explained by oak leaf and twig concentrations. No multivariate explanation of nitrogen levels was found, with a maximum of 32% in the A horizon, exchangeable levels being explained by oak leaf and twig concentrations.

Up to 51% and 72% of soluble magnesium concentrations in the A and B horizons respectively were accounted for by the bracken frond, oak leaf and twig, and litterfall concentrations in the topsoil and bracken and oak in the B horizon. Soluble magnesium was the only ion to show a clear seasonal trend in the data, but other seasonal variables which correlate with oak leaf and twig and bracken frond concentrations may be additionally responsible for the magnesium levels, for example, temperature, potential evapotranspiration and S.M.D. However, the collinearity of the data prevented the assessment of the contribution of these environmental variables. 37% of the variance of soluble calcium levels in the B horizon are accounted for by oak leaf and twig and bracken frond calcium concentrations whilst 60% of the A horizon exchangeable calcium was explained by litter, bracken frond and incident precipitation concentrations.

Table 6.7 shows the significant independent, input and vegetation variables which partially explain the variability in water chemistry, on the hillslope and in surface water. Soil nutrient concentrations were not included in the regression as the aim of the analysis was to discover whether there was a significant relationship between input chemistry, vegetation concentrations and water chemistry.

The relationship between bracken throughfall and soluble phosphorus concentrations in the laboratory soil extract was repeated for the B horizon lysimeter extracts. This fact reinforced the finding that available phosphorus was found in the soil macropores. However, there was no supporting relationship in the A horizon. The exponential decay pattern of sodium concentrations in all lysimeters led to the rejection of multivariate regression results. 51% of chloride concentration in the A horizon lysimeter sample was accounted for by the litter, but again no precipitation variables were significant in the explanation. The regression produced bivariate explanations for nitrogen concentrations at both lysimeter depths, which were 57% by bracken at the 10cm depth and 71% by rainfall at the 25cm depth. No significant relationship for potassium in the 10cm lysimeter sample was found. 92% of the variance in the 25cm lysimeter sample was accounted for by bracken rhizome, oak leaf and twig and oak throughfall concentrations. Litter, litterfall and oak throughfall explain 88% of the variance of magnesium in the 10cm lysimeter extracts, whilst oak leaf and twig, bracken frond and bracken throughfall explain 72% of the variance of magnesium in the 25cm lysimeter samples. The annual growth of oak leaf and twigs explains 71% of the variance in the A horizon sample whereas 85% is explained in the B horizon sample by rainfall and oak leaf and twig. The uptake of calcium, magnesium and potassium by the oak trees partially accounts for the

Table 6.7 **A multivariate explanation of hillslope and surface water chemistry**

	Ca		Mg		Na		K		N		Cl		P	
A horizon lysimeter extract	Oak	71	Litter Otfall Lfall	62 83 88	results rejected		-		Brack	57	Litter	51	-	
B horizon lysimeter extract	Rain Oak	60 85	Oak Brack Btfall	49 64 72	results rejected		Rhiz Oak Otfall	64 81 92	Rain	71	-		Litter Btfall Brack Rhiz	40 56 72 79
Throughflow 3A	-		-		-		Rain	66	-		-		Btfall	99
4A	-		-		-		Otfall Btfall	52 61	-		-		Rain	88
4B	-		-		Oak	94	Rain	67	-		-		-	

Continued..

Table 6.7 Continued

	Ca		Mg		Na		K		N	Cl		P	
Groundwater	Oak	96	Rain Brack	59 80	Bfall	80	-		-	-		Brack Btfall	56 67
Drainage Channel	Rain Otfall	84 97	Brack Btfall Oak Rain	40 52 78 89			Rhiz Otfall Btfall	45 65 73	-	-		-	
Stream	-		-		Otfall Rain Rhiz Lfall	35 51 72 91	Oak Otfall Rhiz Btfall	56 66 78 80	-	Rain	28		

variability in their concentrations in the soil solution of the B horizon. The majority of oak feeder roots were found in the B horizon and their presence may account for the relationships identified.

It was possible to include the throughflow concentrations in a regression equation since the SPSS package facilitated pair wise deletion of missing values. However, the limited data which remains may be misleading. Table 6.7 shows that few significant relationships exist with no explanation for the variance in throughflow sample 3B. Bracken throughfall explained 99% of the variance in phosphorus concentrations in throughflow sample 3A, whilst 88% of the variance of sample 4A was explained solely by rainfall concentrations. These results suggested that the phosphorus content of litter and soil was readily soluble and the phosphorus concentration of throughflow increased proportionately with that of precipitation. The potassium levels in throughflow samples (3A, 4A and 4B) were partially explained by gross and net precipitation inputs, potassium is also readily soluble in water. No other significant correlations were seen for the remaining elements, with the exception of oak leaves and twigs with sodium in sample 4B.

Potassium, nitrogen and chloride levels in the groundwater are not significantly explained by any of the precipitation or vegetation variables. Phosphorus is again related to bracken frond and bracken throughfall concentrations, illustrating the effect of uptake and release of phosphorus from the soil water which flows to the goundwater via macropores. 96% of groundwater calcium concentration is explained by the growth of oak leaves and twigs and this may reflect the extraction of calcium by the deeper rooted trees.

Only calcium, magnesium and potassium levels in the drainage channel have their variability partially accounted for by the independent variables. 73% of the variance in potassium is explained by bracken rhizome concentration and the throughfall inputs. The majority of variance for calcium and magnesium levels were also explained. Rainfall accounted for 84% of the calcium variance with oak throughfall explaining a further 13%. This relationship suggested that gross and net precipitation were responsible for the concentrations of calcium in the drainage channel water, yet Chapter 5 proposed that the channel was supplied by the contributions of lateral flow and the rising water-table. Precipitation inputs with oak leaves and twigs and frond growth explain a total of 89% of the variance in the drainage water of magnesium concentrations. Thus the calcium, magnesium and potassium concentrations in the ephemeral stream suggest a precipitation origin.

The final dependent variable was that of stream water. No significant multivariate relationships were found for calcium, magnesium, nitrogen or phosphorus levels and only 28% of chloride variance was explained by rainfall input. Sodium and potassium, both monovalent cations had 91% and 80% respectively of the variance associated with their concentrations explained. Oak throughfall, rainfall, bracken rhizome and litterfall concentrations explained the majority of the variance in sodium, whilst oak leaf and twig, oak throughfall, bracken rhizome and bracken throughfall account for a large proportion of the variance of potassium. The fact that both cations are monovalent and thus easily leached from the soil, may be a significant factor in explaining these relationships.

In most cases little of the variance in soil and water chemistry could be explained by precipitation and vegetation variables. The environmental variables in Table 6.1 were therefore regressed against vegetation, soil and water nutrient concentrations to determine whether factors such as transpiration, soil moisture deficit or soil temperature were related to nutrient concentrations. No other independent variables were incorporated into the regression at this stage as the analysis sought to initially eliminate those environmental variables which were insignificant in the explanation of ion concentrations within the ecosystem.

Problems of extreme collinearity were encountered at this stage of the analysis. Soil temperature, frond biomass and the S.M.D. were highly intercorrelated at the 99.9% level, whilst rhizome biomass significantly correlated with the monthly A.P.I. at the 95% level. Nie et al (1970) suggest the creation of a new variable which is a composite scale of the set of highly intercorrelated variables alternatively the selection of one variable only, to represent the common underlying dimension. Both of these actions were considered undesirable in this situation as the intercorrelated variables were each thought on a priori grounds to have independent effects on the ecosystem. For example, frond biomass represented the uptake and release of nutrients to the soil, whilst the S.M.D. may have had important effects on soil nutrient concentrations due to the effects of hysteresis.

The environmental variables were first regressed against soil exchangeable ion and soil water chemistry but erroneous results were obtained due to the unreliability of the partial regression coefficients (Johnston, 1980). The technique of multiple regression was not pursued further as it was obvious that certain variables were too closely related to provide a realistic solution. A statistical technique which removed the problems of multiple collinearity was required.

6.1.2. Principal Component Analysis

The statistical technique of principal component analysis rewrites a data matrix into a similar form but in which the new variables are weighted representations of the original set and are uncorrelated with each other. The procedure has three main uses in a study of this type. First, the technique identified intercorrelated variables. Secondly, an underlying pattern of relationships may be identified and the data can be reduced to a smaller set or a single representative variable may be derived. Lastly, the variables are reorganised so that multicollinearity of variables is removed, thus enabling regression to take place. Simple linear correlation coefficients of the original data matrix are converted to cosines and a multidimensional diagram is produced which places all components orthogonal to each other. A new variable or component is derived from the diagram which is an average variable, calculated to be as close as possible to a group of the original variables. All original variables are then correlated with the new component and the squared correlation coefficient of each represents the percentage of the original variable which is explained by the new components. The sum of the squared correlation coefficients for each component is the eigenvalue. Division of the eigenvalue by the total number of original variables provides the percentage of variation of the data set which is explained by the new component. Further components are extracted to explain any remaining variance and the derivation of components is halted when the eigenvalue for the new component falls below 1.0. This action discounts components which account for only a small percentage of the variance which is usually due to idiosyncratic variations in the individual variables (Johnston, 1980).

The SPSS programme offers the facility of varimax rotation of components in the data matrix which aims to simplify component structure, but maintains an orthogonal structure. In some cases a variable may significantly load onto a number of different components and rotation simply serves to highlight the maximum variance which is accounted for. This rotation was used to identify the variables which loaded onto each component. The principal component technique was chosen in preference to factor analysis since components in the former method are exact mathematical transformations of the original variables and all of the variance of the original variables is explained.

It has been shown that each element monitored possesses individual characteristics which make the formulation of general model for the prediction of solute behaviour impossible. Principal component analysis was used in this study to identify ions which may have a similar behaviour within the ecosystem and their association with other variables. For example, sodium and chloride were, in comparison to the other ions monitored, relatively unimportant for plant growth. The concentrations of sodium and chloride throughout the ecosystem were, therefore, thought to be governed by precipitation input and the volume of water moving through the ecosystem, since both ions are readily soluble. It was postulated that all water chemistry variables for sodium and chloride would load onto the same component, whilst vegetation and soil concentrations might be located on different components. Nitrogen, phosphorus and potassium variables would therefore load onto the same component as the vegetation variables, whilst calcium and magnesium concentrations in the ecosystem may be loaded onto the same components as rainfall or soil exchangeable and soluble ion concentrations. Such findings would enable the classification of ion behaviour with the ecosystem.

The principal component technique has been used by several workers to investigate the structure of set of data in an attempt to establish causal relationships. Reid et al (1981) used factor analysis, a very similar technique, to identify controls on precipitation and river water chemistry and also reported that the technique has been successfully used by other workers to identify processes affecting groundwater chemistry and geology.

A separate principal component analysis was performed on the data matrices for each nutrient. All environmental, water, soil and vegetation variables were included in the analysis. No problems of intercorrelation of variables were experienced as the technique rewrites the data matrix to a form whereby the new variables are independent of each other and uncorrelated.

Table 6.8 identifies the percentage of variance which each component explains, for the ions which were monitored in the ecosystem. In general component I represents the group of environmental variables which were known to have pronounced seasonal trends. Figure 6.1 is a diagrammatical representation of Table 6.8 where each proportional sector contains a numerical code for each of the original variables which load onto the respective components. The numerical codes are presented in Table 6.1. It can be seen that no further generalisation to the contents of each component sector can be made as the findings are different for each element. The previous chapter has shown that the behaviour of ions in the ecosystem depends, for example, on their physiological function in plants, valency and origin and therefore each element has produced different variable loadings for each component. The variables which significantly load onto each component are described for each element monitored.

Table 6.8 **Principal components for each chemical element and their percentage explanation**

Ion Component	Ca	Mg	Na	K	N	Cl	P
I	33.7	32.6	31.1	32.8	30.2	30.0	30.1
II	13.5	12.5	14.0	17.4	14.7	15.7	15.5
III	9.4	12.0	12.2	11.8	10.5	12.8	11.9
IV	8.0	7.8	9.0	8.5	7.9	9.2	8.0
V	6.7	6.7	6.9	7.1	7.1	7.6	7.3
VI	6.5	6.0	6.6	5.0	6.1	5.9	5.6
VII	5.6	5.3	5.9	4.9	5.1	4.2	5.2
VIII	3.9	3.6	3.9	3.3	3.6	-	3.8
IX	-	-	-	-	3.6	-	.
Total % explanation	87.3	86.5	89.6	90.8	88.8	85.4	87.4

This table represents the results of 7 separate principal component analyses; components read vertically for each chemical element.

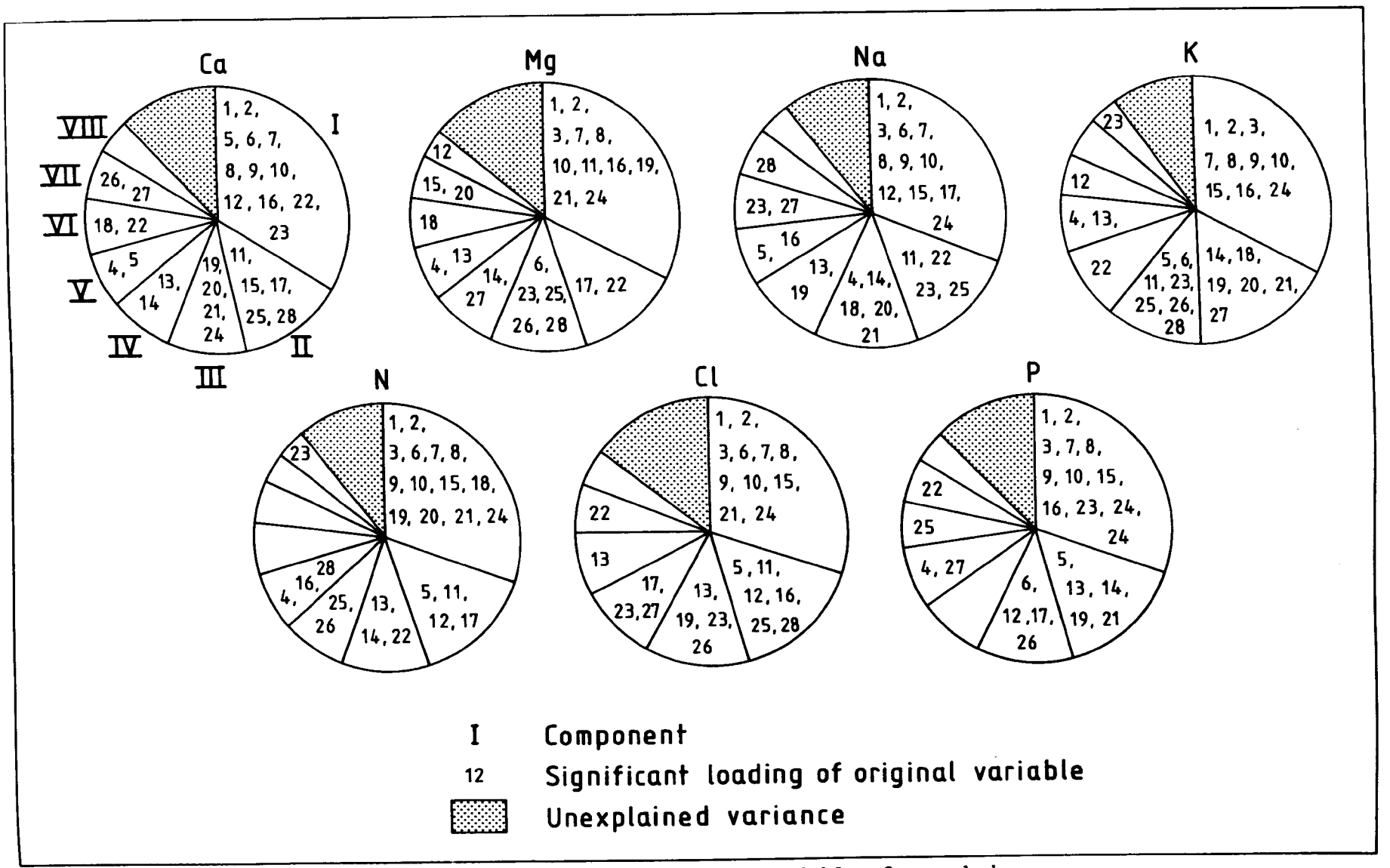


Figure 6.1 Principal components and the significantly loaded variables for each ion

The plot for calcium in Figure 6.1 shows that the chemistry of rainfall, the ephemeral stream and lysimeter samples from the A and B horizons all load onto the first component. The second component contains rhizome biomass and chemistry, litter concentration and the stream calcium content. Component III is made up of three of the soil variables and the bracken frond nutrient content, whilst the fourth component contains the two throughfall inputs. The remaining components are less important in terms of percentage explanation but component VII does contain both of the oak variables, component VI, two of the A soil horizon variables and the fifth component identifies rainfall chemistry and groundwater chemistry. These eight components explain 87.3% of the variance in the data set.

The first magnesium component is composed of most of the environmental variables, the drainage channel chemistry, A and B soil horizon soluble extracts, and the concentration of nutrients in bracken fronds. Component II is comprised of the discharge weighted stream concentration and lysimeter extracts in the A horizon. The third component contains several vegetation variables, rhizome, oak leaf and twig and litter concentrations and also lysimeter extracts from the B horizon. The remaining five components contain the precipitation inputs, exchangeable magnesium and the groundwater concentration. All components explain 86.5% of the variance.

Sodium is the only ion where the volume weighted stream concentration loads onto the first 'seasonal' component. The second component is, like calcium, composed of rhizome biomass and chemistry and also lysimeter extracts from the A and B soil horizons. Three soil variables load on the third component in addition to bracken throughfall and rainfall volume. The last five components contain relatively few significant loadings and the total explanation of variance amounts to 87.6%.

Component I for potassium contains the usual environmental variables of temperature, SMD, stream discharge and PE, but also contains the groundwater and drainage channel concentrations. The second component accounts for a greater percentage of the variance (17.4%) than any of the other second components and contains all soil extracts, bracken throughfall and oak litterfall. The third component is comprised of vegetation parameters such as rhizome biomass and chemistry, oak leaf and twig and litter concentrations as well as effective rainfall, the monthly A.P.I. and a lysimeter extract from 25cm soil depth. The stream concentration is loaded on the fifth variable with oak throughfall and rainfall volume. A total of 90.8% of the variance is accounted for by the eight components.

The first component for nitrogen contains the most variables which include the seasonal variables already identified, plus all soil exchangeable and soluble extracts and the groundwater and drainage channel nitrogen concentrations. The stream concentration is loaded onto the second component with rainfall concentration, rhizome biomass and the monthly A.P.I. The third component comprises lysimeter extracts from both depths and both throughfall inputs. A total of 88.8% of the variance is explained by nine components.

85.4% of the variance in the data for chloride is explained by eight components with rhizome biomass and chemistry, litter, rainfall and the monthly A.P.I. comprising the second component. Oak leaf and twig and oak throughfall make up the third component with two soil variables. The stream concentration is part of the fourth component with litterfall and a lysimeter extract at 25cm soil depth.

Rhizome biomass, groundwater and the ephemeral stream concentrations are all loaded on the first component for phosphorus as well as the environmental variables. Oak and bracken throughfall and the A and B soil horizon soluble extracts are loaded onto the second component with the monthly A.P.I. The third component contains the stream and rainfall input concentration, oak leaf and twig concentration and effective rainfall. A total of 87.3% of the variance was accounted for by eight components.

Whilst each element produces a different sequence of component loadings, an occasional similarity in patterns can be seen. The first component of all elements is composed of those variables with obvious seasonal trends. These are mainly temperature, effective rainfall, SMD, stream discharge, frond biomass and potential evapotranspiration. The concentration of nutrients in the bracken fronds load on all of the first components with the exception of calcium. The concentrations in groundwater and the ephemeral stream are also found in component I for most elements. This finding is probably due to the fact that concentrations were not volume weighted and concentrations showed a significant seasonal behaviour, for example, increased discharge and water levels in winter months diluted concentrations on a seasonal basis. The lysimeter extracts are also loaded onto the first component for several elements, again this location may be partly due to seasonal enrichment by flushing during winter/spring months and the absence of samples during summer months. Component scores form a secondary computer output of the SPSS programme and these scores represent the weighted summed values for the observations of variables over time, the weights being the component loadings. The greater the component score the more representative that observation is of the new component loading. All component scores for the first component of each element exhibited the same pattern, with negative

values occurring for the late autumn, winter months and maximum positive scores in August/September, thus emphasising the seasonal nature of the component.

Rhizome biomass and chemistry and the monthly API individually load onto the same component for several elements whilst the volume weighted stream concentrations for calcium, magnesium and nitrogen, all load onto the second components. The soil exchangeable and soluble ion concentrations show similar component groupings for potassium, calcium, nitrogen. Bracken and oak throughfall are loaded on the same component for calcium, nitrogen and phosphorus. The remaining patterns are specific to each individual element.

The principal component technique has been used so far in this study as a form of classification of variables. Riddell (1970) develops the technique further by incorporating the component scores of each component, with an eigenvalue greater than one, into a multiple regression equation. This development provides a new descriptive expression based on independent uncorrelated variables. The use of this technique assumes all of the original variables have high loadings on their respective components. Johnston (1980) states that overgeneralisation of relationships is very easy, for example, a loading of 0.55 on a component indicates that only 30% of the variance in that variable is associated with the component. Johnston also notes that two variables which have similar loadings on one component but dissimilar on another will therefore be poorly correlated. Sweeping generalisations from the results should therefore not be made. The continuation of this technique using Riddell's (1970) method would therefore have been misleading. Inspection of component loadings for each of the original variables revealed that the majority of percentage explanation by

the new component was low, with an average explanation between 25 and 50%. This level of explanation was clearly unacceptable in the construction of a statistical model.

6.2.0. Conclusion

The search for structure in the organisation of variables within the ecosystem using the statistical analyses described yielded few significant results. The hydrological pathways and solute fluxes within the ecosystem have been identified and flow diagrams summarised by the relative volumes and concentrations found at each stage of the system. However, none of the statistical techniques used were able to statistically relate the concentrations of elements at each stage to such a degree that a statistical model concerning the prediction of solute pathways could be presented. Comparison of these findings with those of other workers was not possible as no similar, extensive analysis could be found in the literature. The results of the principal component analysis showed that the factors which determine the concentration of solutes within the ecosystem are so inextricably mixed that no group of causal processes of variables could be identified for any ion.

Chapter 7.0 CONCLUSION

The multidisciplinary approach to the study of solute pathways in a forested ecosystem has provided a database for the characterisation of nutrient fluxes and stores within a drainage basin. Chapter 1 presented seven working hypotheses which were postulated to test the conceptual biogeochemical model. Results presented in previous chapters were described in more detail whilst this chapter seeks to provide generalised conclusions relating to the investigation, with particular reference to each hypothesis.

Seasonal fluxes in the assimilation and release of nutrients by vegetation were observed for both years of study. The rate of uptake and release varied according to the physiological function of each nutrient. Seasonal behaviour of solute concentrations in the soil and water samples were less apparent than in the vegetation and it was found that the technique of harmonic analysis was inappropriate for identifying such trends. Isolated events such as frassfall or storm litterfall wee shown to be more significant in the input of nutrients than the traditional seasonal inputs of autumnal throughfall and litterfalls. Seasonal trends may therefore be obscured by such events.

Incident precipitation provides an important supply of readily available plant nutrients to the ecosystem. Precipitation chemistry was significantly modified by both the oak and bracken vegetation canopies. All elements, with the exception of nitrogen, showed an overall increase in concentration. The potassium and chloride accumulations in bracken fronds were particularly high and the throughfall concentrations in autumn reflected the mobility of these ions. Those nutrients which were an integral part of the plant fabric were less susceptible to leaching and showed less obvious increases in throughfall concentrations.

The summer troughs and autumnal peaks in soil solute and exchangeable ion concentrations cannot be directly attributed to the uptake and release of nutrients by plants. Factors such as evapotranspiration and autumn 'flushing' may also be responsible. However, solutes contained in the soil water are easily available to plants and most of the water soluble ion concentrations exhibited a pronounced decrease in the spring months of 1981 when rapid uptake of nutrients by oak and bracken was known to occur. Little evidence was observed to attribute changes in soil nutrient concentrations to the frass input. Frassfall occurred in June 1981 and therefore ions were not likely to have been leached from the upper soil horizons. It is suggested that the frass inputs were rapidly dissolved in throughfall and the nutrient rich solution may have been readily drawn upon by the emerging bracken. The production of secondary leaves by the oak following defoliation draws upon nutrient reserves which would normally have been retained for the overall increase in biomass. The level of activity of the defoliating organisms appears to be relatd to winter temperatures and Simpson (personal communication) reports that frass input was minimal in June 1982 following a severe winter, but in June 1983 larval activity was very apparent since the previous winter was relatively mild. Such events emphasise the importance and variability in ecosystem dynamics which relate directly to the release and transfer of solutes. The range of concentrations detected for exchangeable and water soluble ions during the study period were greater than those identified for the spatial variability test. However, the value of results based on laboratory derived soil extracts is questionable in studies of this type since sampling and analytical techniques can introduce a variability which is difficult to characterise and which may obscure events of low magnitude or frequency.

The volume of throughflow which was intercepted was extremely low and therefore it was not possible to assess the influence of vegetation nutrient uptake and release on throughflow solute concentrations. The ionic concentrations in lysimeter extracts exhibited less variability than the laboratory soil extracts since no problems of spatial variability are encountered. However, the two extracts are not directly comparable as lysimeters only withdraw soil water which is held in macropores. Consequently the concentration of nutrients in lysimeter extracts may be more representative of those elements which are mobile within the soil matrix and readily available to plants. The ion determinations for groundwater and the drainage channel were not volume weighted and therefore their concentrations and indeed their presence were largely influenced by seasonal phenomena such as evapotranspiration. The effects of vegetation are therefore indirect since evapotranspiration acts as a regulator to solute movement in the drainage basin.

No consistent evidence could be found to attribute the solute concentrations in stream water to the uptake and release of nutrients by plants or soil nutrient status. However, a short term isolated event, such as frassfall corresponded to an increase in pH and the concentration of certain cations in stream water during June 1981.

The input-output budgets for each nutrient showed that potassium and nitrogen were net gains to the ecosystem whilst all other elements showed net losses. These losses can be attributed to weathering since it was known that no other form of input, such as fertilisers, was contributed to the system. Results also showed that hydrogen was a net gain to the ecosystem. The gradual increase in environmental acidity has unknown repercussions for long term ecosystem stability, but the general indication

from the investigations of other projects is resource degradation. The acidity of the environment may account for the weathering and release of calcium and magnesium from the calcareous bedrock. Calcium and magnesium exhibited significant losses from the ecosystem. It is suggested that the stability of the ecosystem is manifested in the stream water quality since nutrient losses, with the exception of calcium and magnesium, were conservative in comparison to the vast amount of nutrients retained in the basin by nutrient cycling and stores.

Previous studies have inferred that the uptake and release of nutrients by vegetation influences stream water chemistry, but there is no direct evidence to support the hypothesis. The effects of deforestation on stream water chemistry are well documented (Hornbeck et al, 1970) and were described in Chapter 1. However, such research cannot reflect the influence of the growth of natural vegetation since factors such as increased run-off and erosion must also be considered. It has been shown that the present study was unable to isolate a single biogeochemical process which partially explained stream water chemistry, because the results of bivariate and multivariate analyses were inconclusive. The study was, however, able to identify nutrient stores and fluxes for many of the ecosystem processes within the drainage basin and from this information an estimate of the relative stability of the ecosystem was made. Each ecosystem has unique characteristics, for example, vegetation, soil, geology and other physiographic features may vary and therefore it is difficut to make direct comparisons between other semi-natural systems or those which have been manipulated or disturbed by man. It is, therefore, suggested that this study provided a baseline analysis of solute pathways in a semi-natural forested ecosystem. The relative stores and fluxes of solutes are available for comparison with the results of other

similar studies. It is recommended that future research which investigates the influence of vegetation on stream water quality should primarily identify the nutrient stores and fluxes within the ecosystem in order that the magnitude and frequency of solute response in stream water to such seasonal patterns can be more accurately described.

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Dissolved Loads of Rivers and Surface Water
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Biogeochemical controls on river water quality in a forested drainage basin, Warwickshire, UK

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ABSTRACT Spatial variations in river water quality are frequently attributed to differences in vegetation type and density at the mesoscale and microscale, but associations between temporal variations in ecosystem dynamics and river water quality are poorly documented. This paper attempts to identify direct links between monitored hillslope nutrient fluxes and stream solute behaviour over a 19 month period. It is suggested that temporal variability in throughfall chemistry and nutrient assimilation in vegetation and soils are not clearly reflected in seasonal river water quality behaviour.

Controles biogéochimiques sur la qualité de l'eau de rivière en zone forestière, Warwickshire, RU
RESUME Les variations spatiales de la qualité de l'eau des rivières sont fréquemment attribuées aux différences de types et de densité du couvert végétal à l'échelle meso ou micro. Il existe peu d'information sur les associations entre les variations temporelles des écosystèmes et la qualité de l'eau des rivières. La présente communication s'efforce d'identifier les liens directs entre l'étude des flux des substances nutritives de versants et les matières solubles des ruisseaux sur une période de 19 mois. Il apparaît que la variabilité temporelle de la chimie des flux et l'assimilation des substances nutritives dans les sols et dans la végétation ne se reflètent pas directement dans le comportement saisonnier de la qualité de l'eau des rivières.

INTRODUCTION

River water quality reflects the chemistry and volume of precipitation entering a drainage basin, the interaction of ecological, pedological and geochemical processes within the drainage basin and the excess of runoff over rainfall capable of transporting material in solution to river channel networks. The link between the atmosphere, biosphere

and lithosphere is provided by hydrological pathways which control the fluxes of water and dissolved material through the system. Such an explanation of river water chemistry is encompassed in many recent studies of biogeochemical processes in forested ecosystems (cf. Likens *et al.*, 1977; Verstraten, 1977; Reid *et al.*, 1981, Foster & Grieve, 1983). Many authors have identified and quantified temporal variations in throughfall chemistry and nutrient uptake by growing vegetation; in the return of solutes via litterfall and decomposition, and in the nutrient content of soils in isolation (e.g. Carlisle *et al.*, 1966; Gosz *et al.*, 1972; Frankland, 1976; Burt, 1979; Weaver & Forcella, 1979). Direct links between temporal variations in these components and their consequent effect on river water quality have yet to be adequately determined. The apparent complexity of factors governing water chemistry behaviour is not represented in models relating annual or storm-period solute concentrations to instantaneous stream discharge. These simple models often explain a high proportion of variance in the data, although seasonal or nonlinear rating curves may significantly increase levels of explained variance in some cases (Gregory & Walling, 1973; Foster, 1978, 1980). Successful application of such models may imply that direct interactions between hillslope biochemical processes and the streamflow output do not occur over relatively short time periods unless rapid and devastating ecosystem change, such as forest clearance, are identified (e.g. Hornbeck *et al.*, 1970). For these dramatic changes or in cases where spatial variations in background water chemistry may be directly associated with the type and density of vegetation cover (cf. Douglas, 1972; Walling & Webb, 1975), the most important impact may only relate directly to a modification of hydrological pathways and the relative balance of erosion and denudation.

The present study, which is part of a small drainage basin experment designed to trace sediment and solute pathways in a forested ecosystem, attempts to identify direct links between hillslope biogeochemical processes and the quality of river water. The investigation was prompted by previous work (Foster & Grieve, 1983) which has shown the general inadequacy of solute discharge rating curves for predicting river water solute levels.

EXPERIMENTAL AREA AND METHODOLOGY

The experimental area (Fig.1) comprises a small second order drainage basin in north Warwickshire which has been described in detail elsewhere (Dearing *et al.*, 1982; Foster & Grieve, 1983). Data reported in this paper derive from hillslope investigations conducted at site 2 and from river water quality monitoring adjacent to site 1 (Fig.1). The sub-basin to the south and west of the central coniferous plantation is underlain by a variable thickness of boulder clay which overlies the Keele Beds of Upper Carboniferous age. This series is dominated by sandstone and shales, although thin bands of Spirorbis limestone have also been identified by the Geological Survey. Limited outcrops of these deposits in the local area have precluded a comprehensive minerological assessment, but qualitative X-ray fluorescence analyses highlight the most important chemical components of the bedrock (Table 1). Soils of the area have been mapped by Whitfield &

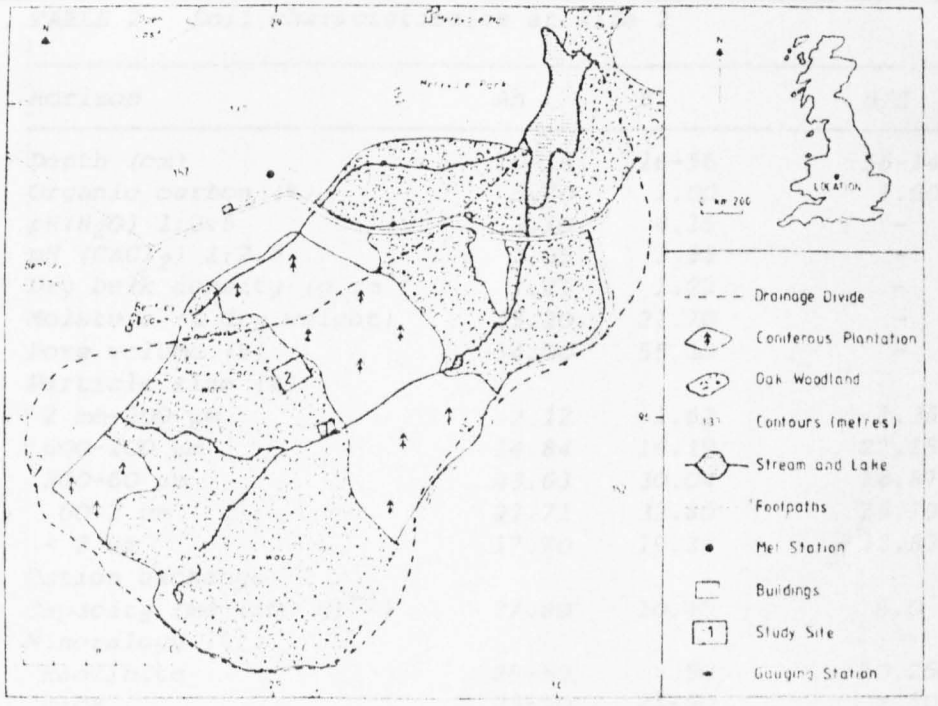

FIG.1 Location of the experimental drainage basin and sampling sites.

TABLE 1 Qualitative X-ray fluorescence analysis of Keele Bed outcrops

	Sandstone	*Shale*
Major element	*K, Si, Ti, Fe*	*Ca, Ti, K, Fe*
Minor element	*Al, Ba, Ca*	*Si, Al*
*Trace element**	*Zr, Rb*	*Ba, Zr, Rb*

**Other trace elements include Mg, P, S, Cl, Cr, Mn, Co, Ni, Cu and Zn.*

Beard (1980) and comprise a Melbourne/Bardsey transition series. The major particle size, minerological and chemical properties of samples collected from site 2 are presented in Table 2. The deciduous woodland is dominated by Oak (*Quercus petraea*), planted in *c.* 1840, with an understorey of bracken (*Pteridium aquilinum*). Silver birch (*Betula pendula*), hazel (*Corylus avellana*) and alder (*Alnus glutinosa*) are also found in the basin, the latter usually confined to narrow flood plain sites where the ground flora is also more diverse.

Detailed analysis of solute pathways was undertaken at site 2 by collection of water, soil and vegetation samples for chemical analysis. Background precipitation chemistry data were obtained from analysis of samples collected weekly at a meteorological station to the north of the basin (Fig.1), and throughfall samples below the oak and bracken canopies were collected in randomly located and orientated 1-m long plastic gutters (Fig.2). Bulked soil samples were collected

TABLE 2 Soil characteristics at site 2

Horizon	Ah	B	B/C
Depth (cm)	10-16	16-56	56-140
Organic carbon (%)	5.70	1.00	1.90
pH(H_2O) 1:2.5	3.70	4.15	-
pH ($CaCl_2$) 1:2.5	3.05	3.25	-
Dry bulk density (g cm^{-3}	1.25	1.22	-
Moisture (% dry weight)	45.20	21.70	-
Pore volume (%)	54.00	55.10	-
Particle size (%)			
2 mm-600 µm	2.12	1.62	1.36
600-200 µm	14.84	16.19	27.15
200-60 µm	43.63	30.04	28.87
60-2 µm	21.71	32.80	29.79
< 2 µm	17.70	19.35	12.83
Cation exchange			
Capacity (me (100 g)$^{-1}$)	27.80	10.40	6.0
Mineralogy (%):			
kaolinite	25-50	> 50	10.25
mica	25-50	25-50	> 50
chlorite	10-25	10-25	5-10
smectite	5-10	5-10	10-25
class	mixed	kaolinitic	mixed
Chemistry (% dry weight):			
N	~~7.70~~	~~5.20~~	~~4.40~~
P X 10^{-3}			

2

from the southern section of the hillslope plot at fortnightly intervals. Litterfall collectors of 1 m^2 area were randomly located beneath the oak canopy and sampled monthly. The oak canopy, bracken fronds and rhizomes were harvested at the same sampling frequency for biomass calculations. Detailed hydrological studies in the same area have included construction of throughflow pits, continuous monitoring of soil moisture tension at 22 locations, weekly monitoring of borehole levels and drainage channel flow and periodic infiltration and dye tracing experiments (Fig.2). In addition to hillslope studies, river water samples were collected at 8-h intervals from the main stream adjacent to hillslope site 1.

All water samples following filtration were analysed by flame photometry, autoanalysis, colorimetry and atomic absorption spectrophotometry. Vegetation samples were digested to provide suitable material for total chemical analysis, and soil samples subjected to soluble and exchangeable extractions as described by Hesse (1971). Although analyses of specific conductace, pH and the concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, NO_3^-, NO_2^-, Cl^- and PO_4^{3-} have been undertaken, this paper concentrates on the biogeochemical processes involved in the cycling of nitrogen, phosphorous, potassium and magnesium only. Input-output budgets for the basin have been reported elsewhere (Foster & Grieve, 1983), and show that approximately one third of incoming precipitation (635 mm) is lost as runoff. Over 90%

FIG.2 Details of instrumentation and sampling sites on the monitored hillslope.

of total steam output comprises dissolved material, and these losses are dominated by Ca^{2+} and HCO_3^- rich waters. It has also been shown that K^+, NH_4^+, NO_3^- and H^+ are a net gain to the basin as a whole and are derived directly from precipitation inputs.

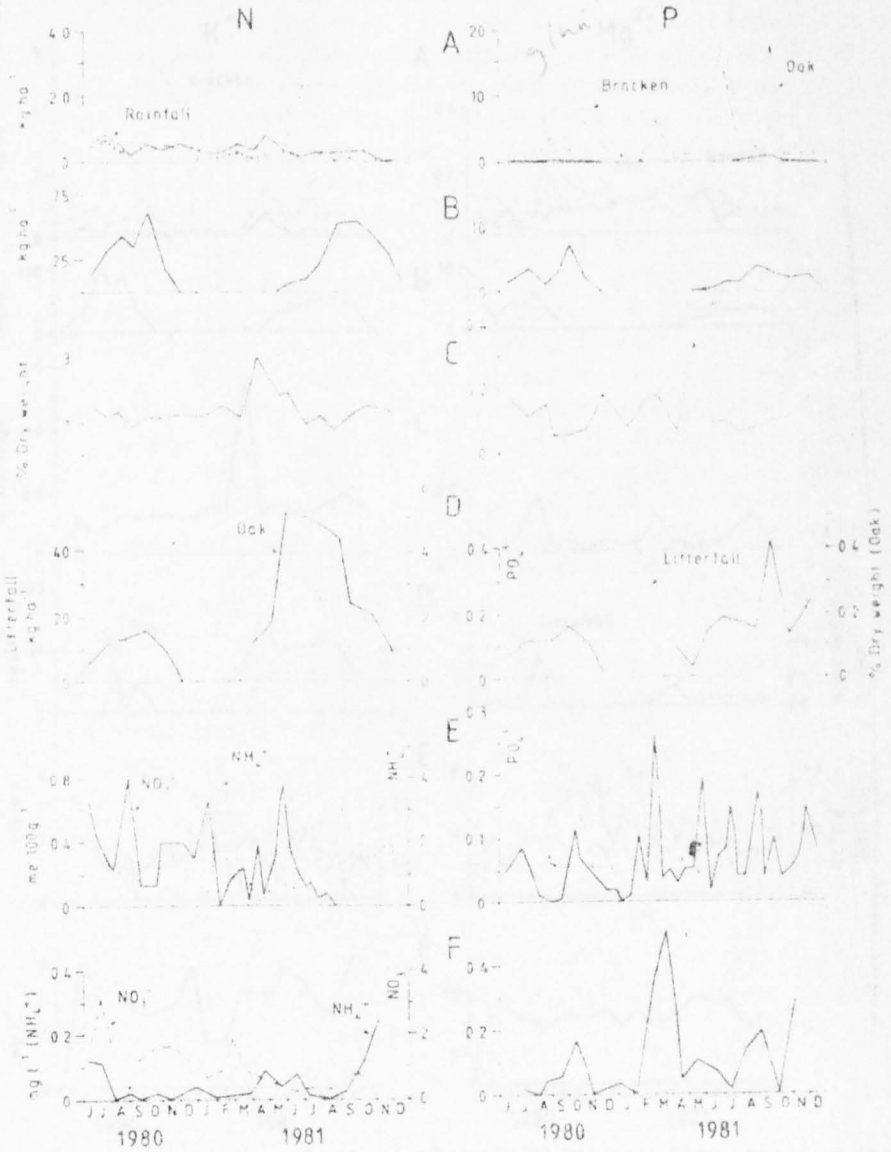

FIG.3 Nitrogen and phosphorous loadings and concentrations (monthly except where stated). (a) loadings in bulk precipitation, oak and bracken throughfall samples (kg ha^{-1}); (b) loadings in the standing crop of bracken fronds (kg ha^{-1}); (c) nutrient concentrations in the soil litter layer (% dry weight); (d) nutrient loadings (kg ha^{-1}) and concentrations (% dry weight) of oak litterfall and harvested oak leaves and twigs respectively; (e) water soluble extracts (NO_3^- and PO_4^{3-}) and exchangeable NH_4^+ in soil Ah horizon (fortnightly samples: me (100 g)$^{-1}$; (f) flow weighted nutrient concentrations in streamflow (monthly average from 8-h samples: mg l^{-1}).

TRENDS IN LOADINGS AND CONCENTRATIONS

Figures 3 and 4 illustrate the trends in the concentration and loadings of the major plant nutrients (N, P and K) and Mg^{2+} in hydrological pathways and the major soil and vegetation storage

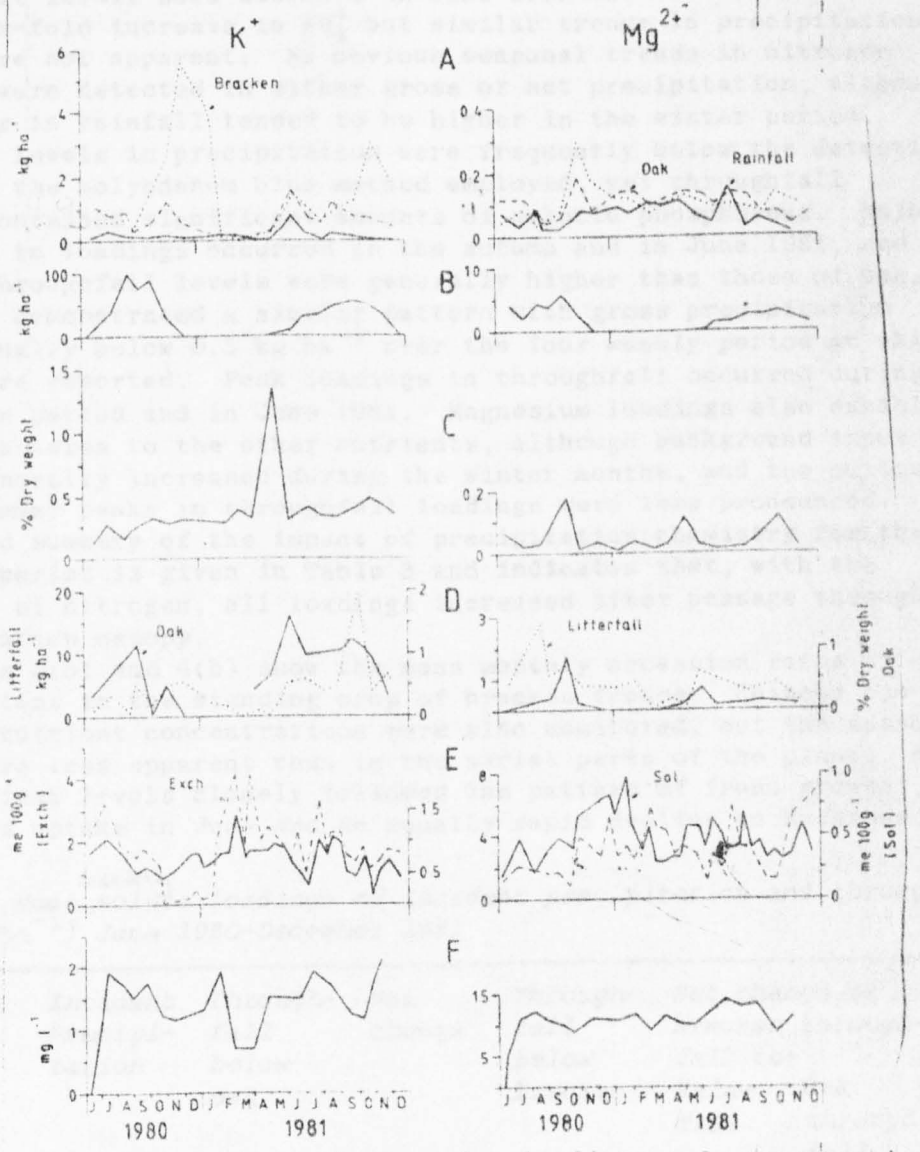

FIG.4 Potassium and magnesium loadings and concentrations (monthly except where stated). (a) loadings in bulk precipitation, oak and bracken throughfall samples (kg ha^{-1}); (b) loadings in the standing crop of bracken fronds (kg ha^{-1}); (c) nutrient concentrations in the soil litter layer (% dry weight); (d) nutrient loadings (kg ha^{-1}) and concentrations (% dry weight) of oak litterfall and harvested oak leaves and twigs respectively; (e) water soluble and exchangeable extracts in soil Ah horizon (fortnightly samples: me (100 g)$^{-1}$); (f) flow weighted nutrient concentrations in streamflow (monthly average from 8-h samples: mg l^{-1}).

components during a 19 month period between June 1980 and December 1981. Inputs from bulk precipitation and subsequent modification in throughfall samples are represented in Figs 3(a) and 4(a). Nitrogen occurs mainly as NO_3 and NH_4^+ in incident precipitation and loadings generally decrease with passage through the vegetation canopy. Peak throughfall levels were detected in June 1981 and were associated with a six-fold increase in NH_4^+ but similar trends in precipitation inputs were not apparent. No obvious seasonal trends in nitrogen loadings were detected in either gross or net precipitation, although NH_4^+ levels in rainfall tended to be higher in the winter period. Phosphate levels in precipitation were frequently below the detection limits of the molybdenum blue method employed, yet throughfall samples contained significant amounts of soluble phosphorous. Major increases in loadings occurred in the autumn and in June 1981, and bracken throughfall levels were generally higher than those of oak. Potassium demonstrated a similar pattern with gross precipitation inputs usually below 0.5 kg ha^{-1} over the four weekly period at which results are reported. Peak loadings in throughfall occurred during the autumn period and in June 1981. Magnesium loadings also exhibited similar patterns to the other nutrients, although background input levels generally increased during the winter months, and the autumn and midsummer peaks in throughfall loadings were less pronounced. A detailed summary of the impact of precipitation chemistry for the sampling period is given in Table 3 and indicates that, with the exception of nitrogen, all loadings increased after passage through the vegetation canopy.

Figures 3(b) and 4(b) show the mean monthly accession rates of each nutrient in the standing crop of bracken fronds. Rhizome biomass and nutrient concentrations were also monitored, but the seasonal trends were less apparent than in the aerial parts of the plant. All four nutrient levels closely followed the pattern of frond growth with rapid uptake in June and an equally rapid decline in November,

TABLE 3 Mean weekly solute loadings of incident precipitation and throughfall (kg ha^{-1}) June 1980-December 1981

Solute	Incident Precipitation	Throughfall below oak	Net change	Throughfall below bracken	Net change of bracken throughfall to: Rainfall	Oak throughfall
Ca^{2+}	0.28	2.8	4.1	+1.3	4.1	+ 1.3	0.0
Mg^{2+}	0.06	0.06	0.11	+0.05	0.12	+ 0.06	+0.01
Na^+	0.26	2.6	2.8	+0.2	3.2	+ 0.6	+0.4
K^+	0.14	1.4	9.7	+8.3	12.6	+11.2	+2.9
NO_3-N	0.16	1.6	1.2	-0.4	1.1	- 0.5	-0.1
NH_4-N	0.19	1.9	1.5	-0.4	2.3	+ 0.4	+0.8
NO_2-N	0.01	0.1	0.3	+0.2	0.1	0.0	-0.2
PO_4-P	0.0	0.0	0.4	+0.4	0.4	+ 0.4	0.0
Cl^-	0.78	7.8	8.8	+1.0	12.3	+ 4.5	+3.5
H^+	0.026	0.234	+0.208	0.150	+ 0.124	-0.084

* divide all values by 10

although magnesium was the least responsive element to changes in biomass. Nutrient concentrations in the soil litter layer are given in Figs. 3(c) and 4(c), and are expressed as a percentage of dry weight. Biomass calculations were precluded by the high spatial variability of litter depth. Nitrogen levels peaked during May and June 1981, but concentrations were relatively stable in the remaining period. Phosphate concentrations exhibited a similar peak and were generally lowest during the autumn months of both years. Potassium and magnesium levels also exhibit midsummer peaks, and significant increases in magnesium were apparent in autumn months. The nutrient loadings of oak litterfall and the nutrient content of harvested oak leaves and twigs are presented in Figs. 3(d) and 4(d). The major litterfall inputs occurred in the late summer and autumn and the summer peak of 1981 represents inputs produced by severe storms. The relative proportion of nutrients in harvested leaves and twigs show a temporal pattern similar to that of bracken fronds. Concentrations increased after budbreak during May and rose rapidly to a maximum in late summer. Magnesium levels were generally lower than those of the major nutrients, but the pattern of rising concentrations during the growth period was still apparent.

Figures 3(e) and 4(e) present trends in soil chemical extracts for the Ah horizon. Water soluble extracts were obtained for NO_3^-, PO_4^{3-}, K^+, and Mg^{2+} and exchangeable extracts for K^+, Mg^{2+} and NH_4^+. Although temporal patterns in all elements, especially phosphorous, were highly variable, broad trends may be identified. High concentrations of NO_3^- and NH_4^+ occur in autumn and midsummer, although the NO_3^- peak generally precedes that of NH_4^+. Exchangeable and soluble K^+ extracts demonstrate a similar pattern, with the former exhibiting a greater amplitude of variation and a dramatic decrease during the winter of 1980. Flow weighted nutrient concentrations in river water samples derived from 8-h sampling and averaged for four weekly periods are given in Figs. 3(f) and 4(f). NH_4^+ levels peaked during the autumn and summer periods, whereas NO_3^- concentrations generally decreased throughout the 19 months of observation with variable peaks in concentration. PO_4^{3-} concentrations peaked in river water samples during the autumn and spring, whereas K^+ levels were generally at a minimum during these periods. Mg^{2+} concentrations exhibited little seasonal variability.

DISCUSSION AND CONCLUSIONS

Rainfall is the main form of precipitation input to the experimental catchment and supplies many essential plant nutrients directly from atmospheric sources. This contribution represents a net gain of nitrogen and potassium to the basin as a whole and has been shown to be important in many ecosystems (e.g. Allen *et al.*, 1968). Seasonal trends in precipitation and throughfall chemistry have been identified for the majority of solutes under consideration in this investigation and discrete inputs are superimposed upon general trends at different times of the year. Similar trends in the precipitation record, obtained by calculation of a monthly antecedent precipitation index (cf. Gregory & Walling, 1973), have not been observed, since convective summer storms maintain a generally uniform rainfall distribution.

Solutes in precipitation are mainly derived from oceanic, terrestrial and anthropogenic sources. Both NH_4^+ and Mg^{2+} demonstrate increased concentrations and loadings during winter months. This trend for the former ion may reflect increased combustion of fossil fuels at nearby power stations, whereas higher winter levels of Mg^{2+} may be related to a predominantly marine origin and to the more frequent occurrence of frontal rainfall which moves into the study area from the west coast of Britain. K^+ and PO_4^{3-} are generally thought to be derived from terrestrial sources, although levels of both ions are low in bulk precipitation input.

The passage of rainfall through a vegetation canopy considerably modifies solute concentrations (Likens *et al.*, 1977) by the washing of surface deposits from vegetation surfaces or by the leaching of labile ions and compounds from within. The latter effect is particularly noticeable during autumn months when cellular breakdown encourages the release of readily available ions before abciasion. This process is especially important in relation to K^+, Cl^-, H^+ and PO_4^{3-}. Increased mobility derives from the physiological role which the nutrient plays in the plant. K^+ and Cl^-, for example, occur as osmotic regulators in cell sap, are therefore not part of the plant fabric and thus may be easily leached. Most ions in throughfall follow the pattern of incident precipitation chemistry during the dormant period with the exception of H^+ concentrations, which increase in winter months and perhaps emphasize the importance of leaf surface leaching by hydrogen ion exchange in summer. Nitrogen is the only nutrient to exhibit a decline in concentrations during passage through the vegetation canopy, and this phenomenon has also been observed in a similar study undertaken by Carlisle *et al.* (1966). Nitrogen is probably absorbed directly by the plant or by microorganisms and algae in the canopy. All ions may be subject to this process but the pattern may be obscured by a greater loss than uptake. The most noticeable feature of the throughfall nutrient data is the peak which occurred for several ions during June 1981. This was attributable to the contamination of water samples by insect frass produced by *Tortrix viridana* larvae and by the larvae of various fly species. Excessive defoliation of the oak occurred for approximately three weeks causing an estimated 60% reduction in oak leaf biomass. A secondary flush of leaves appeared in late June and early July. Other documentary evidence exists in the literature for frassfall in woodland areas (Carlisle *et al.*, 1966), and analysis of a frass sample showed it to be rich in NH_4^+ and PO_4^{3-}. Similar trends were not recorded during June 1982 probably due to the severity of the preceding winter which reduced insect larval populations. The frass input of 1981 proved to be an extremely valuable reference point since naturally enriched inputs to the system could be traced during the summer and autumn months and were immediately followed by rapid nutrient uptake in emergent bracken fronds. Such events also emphasise the importance and variability in ecosystem dynamics which relate directly to the release and transfer of solutes.

Bud break of the oak and the emergence of bracken fronds occurred in mid May and was accompanied by rapid nutrient uptake, especially of nitrogen, phosphorous and potassium. Rapid rates of nutrient uptake in bracken also have been reported by Hunter (1944), Frankland (1976) and Watt (1976). Expression of concentrations of nutrients as

a percentage of dry weight permits assessment of the uptake rate. Between 30 and 50% of nitrogen and potassium, and 70% of phosphorous requirements are taken up during the first four weeks of growth. Maximum biomass and nutrient concentrations are achieved for both bracken and oak in September, followed by a rapid decline attributable to leaching and translocation to rhizomes or other storage organs. Magnesium concentrations do not decline in the same manner and remain in the leaf or frond until abcission. The input of nutrients via litterfall exhibits a distinctly seasonal trend with most input occurring in the autumn. Nutrient rich litter may also be provided throughout the year by inputs of bud scales, flowers and pollen and through the impact of destructive storms, such as those recorded during April 1981. The decomposition of litter in this woodland is probably slow due to the acidity of the soil (pH 3.7-4.2) which is capable of supporting only a limited population of soil fauna and flora. Furthermore, complete bracken frond decomposition may take from eight to ten years because of the high lignin content (Frankland, 1976). A considerable store of nutrients is contained in the litter layer but this can only be released slowly as leaching and decomposition occur. Of the nutrients studied, only magnesium exhibits an increase in concentration, as a percentage of dry weight, in the litter layer during the autumn months.

Most workers have been unable to identify seasonal trends in the nutrient content of soils. This largely reflects the problems of sampling the inherently large spatial variability of the soil (e.g. Frankland *et al.*, 1963; Ball & Williams, 1968), although Weaver & Forcella (1979) have recognized seasonal variations in soil chemistry under six vegetation types in the Rocky Mountains. Several water soluble ions in the present study exhibited significant seasonal variations with peaks in concentration occurring in the winter months. Although depletions of soil nutrient levels have been observed under various agricultural crops (Russell, 1973), in woodland ecosystems nutrients are supplied continuously to the soil from litter and throughfall inputs. Seasonal increases in concentration may therefore relate to rapid decomposition followed by winter leaching of accumulated mineralized material. Soils of the area are dominated by kaolinite which together with the low cation exchange capacity of the B and B/C horizons suggest a nutrient-poor and well weathered soil. Furthermore, exchange sites occupied by major cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) represent less than 10% of cation exchange capacity. Soils on the hillslope site exhibit high permeabilities. Tensiometer and throughflow pit studies have shown that lateral water movement within the soil matrix is a rare phenomenon, which only occurs when soil water levels approach saturation throughout the profile. Most water percolates to a clay layer located at 140 cm depth and forms a perched water table. Subsurface flow occurs downslope towards the main stream and a small ephemeral drainage channel where flow is controlled by fluctuations in groundwater levels.

Volume weighted river water concentrations draining the entire deciduous woodland area do not exhibit marked seasonal trends, and the fluctuations in nutrient levels in the hillslope subsystem are not generally apparent in the river. Small increases in K^{+} and Mg^{2+} concentrations occur in June following the period associated with frass inputs, whereas peak nitrogen and PO_4^{3-} levels are related to

times of maximum runoff. No single hillslope biogeochemical process may therefore be identified as exerting a controlling influence on river quality behaviour, although isolated events may affect concentrations in the short term. The overall interaction of the ecosystem masks the seasonal influence which vegetation and soils have been shown to exert on hillslope water chemistry. The apparent elimination of such patterns in river water may reflect the buffering effects of the narrow flood plain (Foster & Grieve, 1983) and the impact of groundwater chemistry on the river water quality in this area. Furthermore, since solute concentrations in river water are volume weighted, the high winter PO_4^{3-} outputs may be associated with erosional processes rather than biogeochemical cycling, which is in direct contrast to the behaviour of K^+ and Mg^{2+}.

Detailed chemical analyses have been undertaken in many components of this forested ecosystem and hillslope biogeochemical interactions may be identified. Few of the hillslpe variables, however, correlate directly with river water behaviour but individual events can be seen to exert some influence. This finding may have an important bearing on the future modelling of water quality dynamics in this and other similar areas.

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The use of specific conductance in studies of natural waters and soil solutions

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ABSTRACT Specific conductance (SC) is widely used as a measure of mineral salt concentration and a variety of models have been employed which relate SC to total dissolved solids (TDS) and individual ionic concentrations. This paper attempts to evaluate several models and highlights two major problems associated with them from analysis of water samples collected from two small catchments in East Devon and North Warwickshire. First, the presence of dissolved organic material, at the levels encountered in soil solutions, may seriously affect the SC/TDS relationship and will often be an undetected component of dissolved load. Secondly, the low pH of some water samples is shown to affect those models which calculate SC on the basis of individual ionic concentrations. This results from high H^+ ion levels and associated increased solubility of other ions, such as Fe^{3+}, Al^{3+} and Mn^{2+} which are not normally determined in water quality studies.

Emploi de la conductance spécifique dans les études des eaux naturelles et des solutions dans le sol

RESUME La conductance spécifique (SC) est largement utilisée comme mesure de la concentration en sels minéraux et on a employé divers modèles qui rattachent SC au poids total de solides dissous (TDS) et aux concentrations ioniques individuelles. Cet article tente d'estimer la valeur de plusieurs modèles et met en lumière deux problèmes importants qui leur sont liés, en utilisant les analyses des échantillons d'eau prélevés sur deux petit bassins dans l'est du Devon et le nord du Warwickshire. Premièrement, la présence de matières organiques dissoutes, au niveau que l'on rencontre habituellement dans les solutions dans le sol peut influencer sérieusement le relation SC/TDS et sera souvent un constituant de la charge dissoute qui n'est pas décelé. En second lieu, le faible pH de certain

échantillons d'eau affecte comme on le démontre ici les modèles qui calculent SC sur la base de concentrations ioniques individuelles. Ceci résulte du haut niveau en ion H^+ et de l'augmentation de solubilité qui lui est associée pour d'autres ions, tels que Fe^{3+}, Al^{3+} et Mn^{2+} dont la concentration n'est pas normalement déterminée dans les études de qualité de l'eau.

INTRODUCTION

Specific conductance (SC) has been widely used as a measure of mineral salt concentration in both natural waters and soil solutions (e.g. Toler, 1965; Steele, 1968, 1976; Hem, 1970; Walling & Webb, 1975; Foster, 1978a). The major advantage of this measure is that it can be obtained on a continuous basis in rivers using simple and inexpensive monitoring equipment (Gregory & Walling, 1976) and therefore permits the detection of short term changes in water chemistry behaviour which may not be observed using a discrete sampling framework. In addition, SC is often used to obtain estimates of the total dissolved solids (TDS) load of a stream which is important in catchment denudation studies (e.g. Walling, 1978; Foster, 1980). This is achieved by empirically determining TDS/SC relationships for selected river water samples, and estimating TDS from the continuous SC record.

The relationship usually takes the form

$$TDS = a + k\ SC \tag{1}$$

where a and k are constants (Walling, 1974). Since the conductivity of pure water is zero, equation (1) should reduce to:

$$TDS = k\ SC \tag{2}$$

However, many studies indicate that the constant, a, in equation (1) is significantly different from zero, which may result from non-linearity of the relationship at a high SC (e.g. Hem, 1970). The value of k usually lies between 0.55 and 0.75 (Gregory & Walling, 1976) which reflects the variable ion balance in natural waters since the limiting ionic conductance is not the same for each individual ion or ion pair (Robinson & Stokes, 1968). Ledbetter & Gloyna (1964) express the SC/TDS relationship in quadratic form although this model has been little used in recent literature.

More recently, Steele (1968, 1976) has advocated the use of SC as a measure of ionic concentration, of the form:

$$C_i = a + k\ SC \tag{3}$$

where C_i is the concentration of the ith ion. The intercept, a, was found to be significantly different from zero in most cases. McNeal *et al.* (1970) employ a similar model to calculate the SC of single salt solutions under laboratory conditions. To calculate the conductivity of mixed salt solutions they suggest that the constant, a, is weighted by the proportion (in meq l^{-1}) of cations and anions in the sample. This simple model was compared with both third order polynomial and exponential models and found to produce consistent results.

An alternative model for calculating SC from individual ionic

concentrations was presented by Tanji & Biggar (1972):

$$SC = \Sigma_{i=1}^{n} li = \Sigma_{i=1}^{n} \lambda_i C_i \quad (4a)$$

where

$$\lambda_i = \lambda_i^o - AC_i^{\frac{1}{2}} \quad (4b)$$

li is the ionic SC ($\mu S\ cm^{-1}$),
C_i is the concentration of the ith ion (meq l^{-1}),
λ_i is the limiting ionic conductance (cm^2 equiv Ω),
λ_i^o is the limiting ionic conductance at infinite dilution (cm^2 equiv Ω),
A is a constant.

The specific conductance of natural waters is not simply a function of dissociated ionic species, but is complicated by changes in pH and the presence of organic material in solution. Robinson & Stokes (1968) suggest that the dissociation of water molecules below a pH of approximately 6.5 may affect the calculations of SC, although none of the models outlined above account for this. The presence of organic material in solution will also affect TDS, and Hobbie & Likens (1973) and Arnett (1978) have shown the contribution of organic material to dissolved load. This contribution is likely to be higher in throughfall, particularly in summer (Malcolm & McCracken, 1968), and in water moving laterally through the soil.

Organic matter in solution consists of water-soluble nonhumic substances and fulvic acids (Schnitzer, 1976). The former are relatively easily attacked in the soil and have a short survival rate, and hence fulvic acids form the bulk of dissolved organic material in most natural surface waters (Schnitzer & Khan, 1972; Gjessing, 1976), although Malcolm & McCracken (1968) identified polyphenols and sugars in throughfall.

Fulvic acids have a pH-dependent net negative charge (Black & Christman, 1963; Gjessing, 1976), and, while no systematic measurements of this charge have been made for different locations, Gjessing (1976) suggests that the humus transported by water is of low exchange capacity. Of the water-soluble nonhumic substances, carbohydrates are by far the most significant group. These also possess a pH-dependent charge, resulting from ionization of carboxyl groups (Lowe, 1978).

Thus dissolved organic material in natural water consists of weakly charged compounds and this relative contribution to SC is likely to be very much lower than to TDS, especially when contrasted with the major cations and anions in solution. Also since organic material is capable of adsorbing metal cations (Gjessing, 1976) it may even reduce SC.

The objectives of this paper are firstly, to evaluate the TDS/SC models outlined above, and secondly, to examine the effects of pH and the presence of dissolved organic material on TDS/SC relationships.

MATERIALS AND METHODS

Water samples for chemical analysis have been obtained from two areas. First, river water samples were collected from a small

cultivated basin in East Devon from the main stream and three sub-basins; a tile drain, drainage ditch and a woodland stream unaffected by cultivation. Described in detail elsewhere (Foster, 1978a) the basin is underlain by Permian breccias, conglomerates and sandstones and, with the exception of 14% of mixed deciduous woodland dominated by oak (*Quercus robur*) and ash (*Fraxinus excelsior*), is primarily devoted to cereal production. In addition, bulk precipitation samples were collected over the same period from 1974 to 1976.

Secondly, water samples were collected from a variety of locations in a forested basin in North Warwickshire. Weekly samples were obtained from the main stream and from throughfall beneath the tree canopy during 1978 and 1979. In addition, vacuum water samplers, as described by Parizek & Lane (1970), were employed to collect samples from the unsaturated soil zone at three locations from a slope adjacent to the main stream; the flood plain, the flood plain/valley side junction and the valley side slope. Geologically, the area comprises boulder clay overlying Keele Beds (Upper Coal Measures), and the vegetation canopy is dominated by oak (*Quercus petraea*) with a bracken (*Pteridium aquilinum*) understory on the valley side slopes and alder (*Alunus glutinosa*) with a bramble (*Rubus sp*) understory on the flood plain.

All samples were analysed for SC, corrected to 25°C, and pH. After filtering through Whatman GF/C glass fibre filter papers, the major cations Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}, were determined by flame photometry and by atomic absorption spectrophotometry. The anions Cl^{-} and NO_3^{-} were determined on an autoanalyser. Selected samples were analysed for SO_4^{2-} using an autoanalyser, HCO_3^{-} and CO_3^{2-} by titration and Fe^{3+}, Al^{3+} and Mn^{2+} by atomic absorption spectrophotometry. TDS was determined by evaporating to dryness at 105°C.

Dissolved organic matter was determined as chemical oxygen demand on aliquots of filtered samples evaporated to dryness. The technique is similar to that described by Maciolek (1962), using wet oxidation by potassium dichromate and concentrated sulphuric acid followed by back titration with ammonium ferrous sulphate. Due to the low concentration of organic material, and the small samples available, the strength of the potassium dichromate was M/60 and of the ammonium ferrous sulphate M/20. The correction for Cl^{-}, given by Hesse (1971), for soil samples, was tested empirically and found to be adequate over the range of concentrations encountered. Oxygen consumed was converted to DOM assuming an oxygen equivalent of 1.44 (Maciolek, 1962). The samples examined for organic material were obtained only in North Warwickshire, and included the stream, soil water and summer throughfall samples, but were collected over a longer time period. Separate SC/TDS relationships were calculated for these samples.

THE TDS/SC RELATIONSHIP

Applicability of equation (1)

Samples for total dissolved solids determinations were obtained from the river water samples collected in East Devon (22 samples) and North Warwickshire (26 samples). The general relationship based on

equation (1) for both sets of samples was good, with correlations in excess of 0.9 (Table 1). However, in both cases the intercept (a) was significantly different from zero and the North Warwickshire samples demonstrated a low regression coefficient. Attempts were made to fit the Ledbetter & Gloyna (1964) quadratic model to both sets of data, but no significant improvement in levels of explained variance was achieved.

The effects of organic material

Dissolved organic matter (DOM) was included in stepwise multiple regression models to examine its significance in explaining TDS variations. Results of analysis for the stream, summer throughfall and slope soil water are given in Table 2.

In the samples from the stream, means and standard deviations of DOM were low (4.43 and 2.25 mg l^{-1} respectively). The bivariate regression model was similar to that quoted previously for the more

Table 1 TDS/SC relationships for river water samples

Site	a	k	SE	R^2	Significance level (P<)
East Devon	22.160	0.685	8.38	96.0	0.001
North Warwickshire	110.17	0.476	22.62	85.0	0.001

Model form as equation (1), TDS = a + k SC.
SE = standard error of intercept; R^2 = coefficient of determination.

Table 2 Effect of DOM on the estimation of TDS from SC (North Warwickshire data)

Correlation matrices

	Stream (N = 46)		Throughfall (N = 35)		Soil water (N = 48)	
	TDS	DOM	TDS	DOM	TDS	DOM
SC	0.841***	−0.059	0.793***	0.530**	0.854***	0.256
TDS		−0.074		0.403*		0.530***

Simple linear regression

Site	Equation	SE	R^2	Partial with DOM
Stream	TDS = 106.71 + 0.48SC	30.88	70.8***	0.095
Throughfall	TDS = 23.00 + 0.70SC	16.22	62.9***	−0.033
Soil water	TDS = 40.79 + 0.68SC	73.00	73.0***	0.625***

Multiple linear regression

Site	Equation	SE	R^2	R^2 increase
Soil water	TDS = 11.5 + 0.61SC + 1.09DOM	29.45	83.7	10.7

SE = stand error of intercept; R^2 = coefficient of determination.
Significance levels: *P<0.05, **P<0.01, ***P<0.001.

restricted data base, although R^2 was slightly reduced. The partial correlation of TDS and DOM, controlling for SC was insignificant and the multiple regression model only explained 0.2% more variance than the bivariate model. Similarly, the multivariate model for throughfall did not produce a significant correlation, and although DOM levels were slightly higher in these samples (18.00 mg l^{-1}) than the stream they demonstrated a similar low variability (6.00 mg l^{-1}).

DOM levels in the soil water samples, however, were high with a mean of 39.7 mg l^{-1}, and ranged from 14.3 to 99.6 mg l^{-1}. The simple linear model explained 73% of the variance in the data, and the partial correlation model was also significant, increasing levels of explained variance by 10.7%. The intercept for the multiple regression model was brought much closer to zero, since one important reason for a nonzero intercept is the presence of non-ionized dissolved material. This effect of DOM on the TDS/SC relationship is shown graphically in Fig. 1. In the case of throughfall, the regression line intercept was not significantly different from zero, but the nonzero intercept in the stream analysis may reflect either nonlinearity at high solute concentrations (ion pairing) or the presence of other non-ionized substances (e.g. silica).

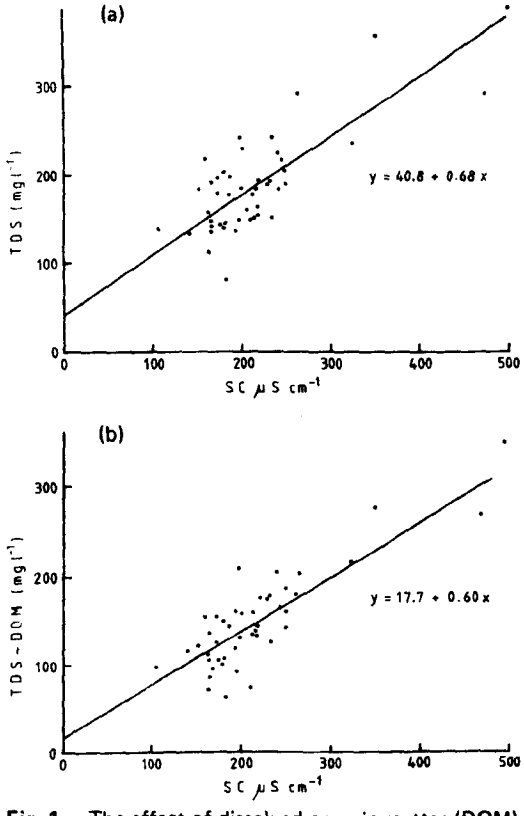

Fig. 1 The effect of dissolved organic matter (DOM) on the TDS/SC relationship for soil water samples collected in North Warwickshire: (a) TDS uncorrected for DOM, (b) TDS corrected for DOM.

ION/SC RELATIONSHIPS

The model presented by Steele (1976), equation (3), was applied to both East Devon and North Warwickshire samples (Table 3). The

Table 3 Estimation of ion concentration from SC by linear regression

	a	k	SE	R^2	a	k	SE	R^2
East Devon samples								
	Main stream (N = 998)				Woodland stream (N = 70)			
K^+	6.75	−0.010	0.001	9.6***	1.24	0.003	0.004	22.9***
Ca^{2+}	6.35	0.060	0.003	59.8***	−0.69	0.077	0.005	77.7***
Na^+	1.13	0.041	0.001	75.7***	9.21	0.032	0.005	38.7***
Mg^{2+}	−9.08	0.053	0.0004	88.5***	1.07	0.021	0.001	89.3***
Cl^-	20.54	0.024	0.001	16.4***	20.26	0.036	0.009	19.5***
NO_3^-–N	8.74	−0.011	0.001	6.8***	3.03	−0.001	0.001	21.7***
	Tile drain (N = 48)				Drainage ditch (N = 30)			
K^+	9.84	−0.026	0.008	18.8**	16.82	−0.031	0.009	29.2***
Ca^{2+}	17.88	0.162	0.018	64.8***	−12.86	0.127	0.011	81.0***
Na^+	3.07	0.014	0.005	13.4**	5.51	0.017	0.003	51.3***
Mg^{2+}	−0.68	0.015	0.003	42.0***	0.12	0.018	0.006	31.7***
Cl^-	8.84	0.027	0.016	5.7	4.43	0.061	0.013	42.1***
NO_3^-–N	0.94	0.014	0.016	1.6	−15.28	0.067	0.013	47.5***
	Bulk precipitation (N = 67)							
K^+	−0.71	0.028	0.004	37.5***				
Ca^{2+}	0.38	0.017	0.003	34.8***				
Na^+	1.55	0.017	0.009	5.5				
Mg^{2+}	0.14	0.006	0.001	16.9***				
Cl^-	2.66	0.036	0.011	14.2***				
NO_3^-–N	0.42	0.004	0.002	4.9				
North Warwickshire samples								
	Main stream (N = 25)				Flood plain (N = 60)			
K^+	1.50	0.003	0.002	8.8	0.57	0.005	0.002	13.2**
Ca^{2+}	25.77	0.038	0.019	13.7	−17.41	0.093	0.011	57.2***
Na^+	15.09	0.009	0.015	2.0	9.31	0.012	0.005	9.0*
Mg^{2+}	1.30	0.018	0.005	37.9***	15.36	0.007	0.005	3.4
Cl^-	38.70	0.009	0.026	0.5	44.24	−0.027	0.014	5.9
NO_3^-	21.57	−0.026	0.009	27.0**	−27.26	0.104	0.031	16.2**
	Flood plain/slope junction (N = 25)				Valley slope (N = 72)			
K^+	5.27	0.001	0.001	1.7	11.47	−0.001	0.009	0.0
Ca^{2+}	−0.26	0.073	0.008	79.2***	0.58	0.003	0.003	1.8
Na^+	−7.48	0.051	0.007	67.1***	−29.73	0.187	0.020	55.2***
Mg^{2+}	0.05	0.038	0.003	86.9***	0.30	0.009	0.003	10.2**
Cl^-	−13.32	0.088	0.012	69.2***	1.30	0.059	0.014	19.6***
NO_3^-	97.55	−0.172	0.051	33.1**	4.05	0.015	0.013	2.0
	Throughfall (N = 125)							
K^+	−6.70	0.108	0.009	52.0***				
Ca^{2+}	1.15	0.018	0.001	59.9***				
Na^+	−0.28	0.034	0.003	49.0***				
Mg^{2+}	0.10	0.009	0.002	20.4***				
Cl^-	−1.167	0.051	0.007	29.8***				
NO_3^-	0.96	0.014	0.002	20.3***				

Model form as equation (3), $C_i = a + k\,SC$.
SE = standard error of slope; R^2 = coefficient of determination.
Significance levels: *P<0.05, **P<0.01, ***P<0.001.

majority of relationships were significant, although the constant, a, in most models was significantly different from zero. Similarly the slope, k, appeared to vary significantly from site to site. In order to establish the applicability of general ion/SC relationships for areas of similar lithology, the computed values of k, in equation (3), were compared by testing for interaction in analysis of covariance models (Snedecor & Cochran, 1967). For each SC/ion regression, slopes were significantly different ($P < 0.001$) among the five subcategories at both sites for all ions. When the throughfall and bulk precipitation samples were omitted, the slopes remained significantly heterogeneous, with the exception of K^+ for the Warwickshire site. General models of the form of equation (3) were therefore invalid at both of these small catchments, and it must be concluded that the model constants are specific to individual sources of water.

Subsequent analysis of these data was undertaken by substituting the value of C_i in equation (3) by the sum of major cations in solution. (ΣC_i^+ meq l^{-1}) and the model re-evaluated (Table 4). The sum of anions was not used since major anions were not determined in all available samples. Analysis suggests an improved model fit with higher levels of explained variance. Comparison of slopes, however, again yielded highly significant differences ($P < 0.001$) within the two sites even when throughfall and rainfall data were omitted, suggesting again that models of the form of equation (3) are specific to individual sources of water.

Table 4 Estimation of total cation concentration from SC by linear regression

Site	a	k	SE	R^2	Significance level ($P<$)
East Devon					
Main stream	−0.36	0.009	0.0001	92.3	0.001
Woodland stream	0.49	0.007	0.0003	90.8	0.001
Tile drain	−0.56	0.009	0.0009	70.0	0.001
Drainage ditch	0.04	0.008	0.0006	79.1	0.001
Bulk precipitation	0.08	0.003	0.0002	24.4	0.001
North Warwickshire					
Main stream	2.09	0.004	0.001	26.9	0.001
Flood plain	0.81	0.006	0.001	45.3	0.001
Flood plain/slope junction	−0.20	0.009	0.0005	91.0	0.001
Valley slope	−0.95	0.009	0.001	65.9	0.001
Throughfall	−0.118	0.006	0.0003	70.4	0.001

Model form as Table 3.
SE = standard error of slope; R^2 = coefficient of determination.

As an alternative to the field derived model presented by Steele (1976), the McNeal *et al.* (1970) model was evaluated for 72 samples where, in addition to the routinely analysed ions, data for SO_4^{2-}, HCO_3^- and CO_3^- were also available. These samples from the North Warwickshire area were selected from all sites and covered a range of pH values from 3.56 to 7.85. The method estimates SC from empirically derived SC/C_i relationships for single salt solutions developed in the laboratory, where the sum of conductivity values

for each ion provides an estimate of SC for the mixed sample. Comparison of measured and calculated SC values indicated a high correlation of 0.94 (Fig. 2). This relationship was improved by including pH in a partial correlation model ($r = 0.57$) which was significant at the 0.001 level and increased explained variance to 94.88%. The significance of pH is probably related to two major factors; firstly, the increased H^+ ion concentration at low pH which will contribute to measured SC, and secondly, the much lower concentration of ions in solution at low pH values.

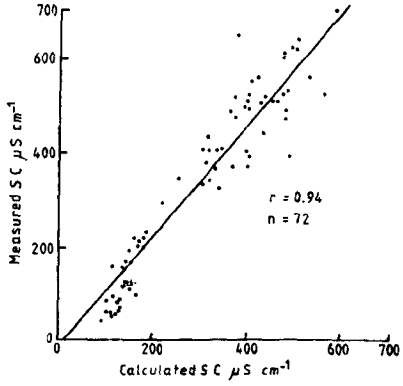

Fig. 2 Relationship between measured and calculated SC using the method of McNeal *et al.* (1970).

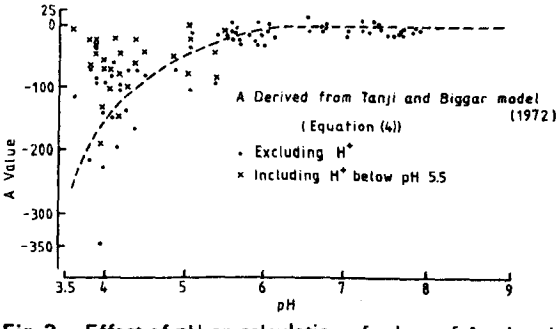

Fig. 3 Effect of pH on calculation of values of A using the method of Tanji & Biggar (1972).

The effect of pH was investigated in greater depth with reference to the model presented by Tanji & Biggar (1972). This model (equations (4a) and (4b)) estimates SC from the concentration of a particular ion in solution weighted by its limiting ionic conductance. Values for A in equation (4b) of between 4 and 9 used by Tanji & Biggar were found to result in a poor estimate of measured SC. Estimates of A were therefore obtained by substituting equation (4b) into equation (4a) and using measured SC as the best estimate of total conductivity. Estimates of A ranged from 11.3 to -340.8 on the basis of nine major ions in solution, K^+, Ca^{2+}, Na^+, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}, HCO_3^- and CO_3^{2-}, and using estimates of λ_1^0 from Robinson & Stokes (1968). The high negative values appeared to be strongly related to pH which was not included in the original

model (Fig. 3). H^+ has a high limiting conductivity of 349.8 which adds in excess of 100 μS cm^{-1} at a pH of 3.5, but reduces to less than 0.2 μS cm^{-1} at a pH of 6.5. Recalculation of A values including H^+ at pH values of less than 5.5 significantly reduced the large negative values (Fig. 3), but still generally remained lower than estimates obtained from samples above a pH of 5.5. H^+ ion concentration is, therefore, not the only explanation for high residual A values.

At low pH values recorded in the soil and throughfall systems other ions, especially Fe^{3+}, Al^{3+} and Mn^{2+}, are soluble. Further investigation of 27 samples revealed high levels of all three ions in certain parts of the system, notably the acid slope and throughfall samples. An estimate of contributing conductivity from these ions was obtained using laboratory prepared solutions with concentrations ranging from 0.1 to 10 mg l^{-1}. Calculation of conductivity attributed to the anions in solution was achieved using the Tanji & Biggar model with a constant value of 5.5. SC attributed to Fe^{3+}, Al^{3+} and Mn^{2+} was found by subtraction.

Recalculation of the A values from the 27 samples re-analysed indicated a significant reduction in the negative values previously encountered from solution of this equation (Fig. 4). Several samples at low pH indicate higher values than would be expected from other samples taken in the same area. This may be related to two factors: firstly, no account was taken of the effect of H^+ concentrations when estimating the contribution of Fe^{3+} to overall SC in laboratory analyses, and secondly, it was assumed, for purposes of calculating A values, that Fe^{3+} was in solution. Many authors (e.g. Hem, 1970) have suggested that Fe^{3+}-organic matter complexing

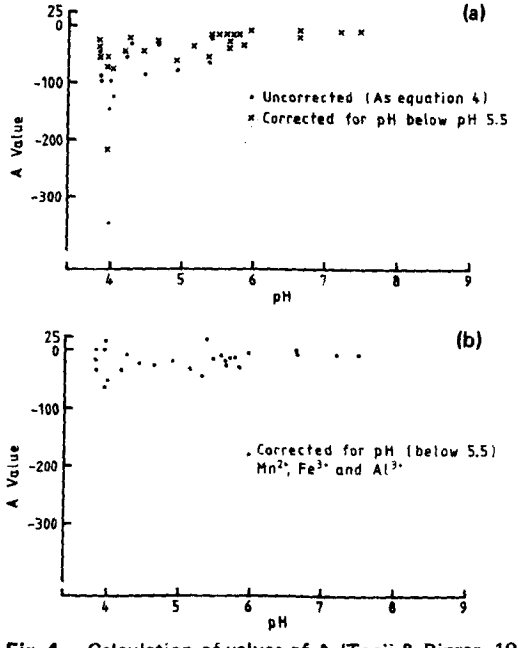

Fig. 4 Calculation of values of A (Tanji & Biggar, 1972): (a) corrected for pH, (b) corrected for pH and the concentrations of Mn^{2+}, Fe^{3+} and Al^{3+}.

occurs in natural waters and soil solutions, although there is no direct relationship between colour intensity caused by organic staining and Fe^{3+} concentrations. This complexing would result in a reduction of SC attributable to Fe^{3+} in solution, although no attempt was made to estimate relative proportions of free:chelated Fe^{3+} for samples analysed in this study.

DISCUSSION AND CONCLUSIONS

In the absence of non-ionized material and above a pH of around 5.5, SC is considered to be a useful measure of TDS for routine water quality analysis. Regression relationships in the form of equation (1) may be used to explain high proportions of variance in TDS loads. On the basis of evidence presented here the levels of DOM in stream water and in throughfall were too low and displayed too little variability to be of significance in affecting the SC/TDS relationship. However, the soil water samples did have sufficient variation in DOM to influence the regression relationship and DOM must be considered in estimation of dissolved load carried in soil solutions. It may also be of significance in streams draining moorland catchments where DOM levels have been found to be very much higher than those reported here (Arnett, 1978).

The nonzero intercept, often encountered in TDS/SC relationships (Hem, 1970) may be interpreted as resulting from either nonlinearity (ion pairing) at high concentrations or the presence of non-ionized dissolved material. Of major importance in this context is the presence of silica which, for the North Warwickshire stream, was of approximately 10.0 mg l^{-1} SiO_2. Inclusion of this value with average dissolved organic material values of approximately 7.0 mg l^{-1} accounts for between 15 and 20% of the regression intercept value. For the East Devon main stream average SiO_2 values of approximately 20 mg l^{-1} have been reported (Foster, 1980), which accounts for over 90% of the regression intercept.

The SC/ion models advocated by Steele (1976) are considered to be relatively poor general models for three reasons. First, low levels of explained variance were obtained for some ion/SC relationships. Secondly, the model contains the implicit assumption that all ions respond to changes in hydrological conditions in the same way. This has been shown to be invalid at both the seasonal and individual storm level for the East Devon catchment (Foster, 1978a, 1978b). Thirdly, it has been shown that the constants of equation (3) are significantly different for individual ions at different sites, even within the same general area. Application of this model is therefore unlikely to be very useful for detailed investigations of water and soil water chemistry behaviour, and it is suggested that SC should only be used as an indicator of water chemistry response rather than a predictor of individual ionic concentrations.

Attempts to calculate SC from consideration of the properties of simple solutions were relatively successful, although improvements in the McNeal *et al.* (1970) model were achieved by including pH in a partial correlation model, accounting for almost 95% of the variance in the data. This improvement probably reflects the

generally lower ionic concentrations in more acid samples. Similar conclusions may be drawn from the Tanji & Biggar (1972) model where, at low pH, estimates of A were significantly improved by including an estimate of hydrogen ion concentration. Further improvements resulted from consideration of the effects of iron, aluminium and manganese whose solubility at low pH is greatly enhanced. It is therefore suggested that the Tanji & Biggar (1972) model is only of use over a limited pH range unless consideration is given to both the direct and indirect effect of pH.

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